COMPOSITIONAL AND SENSORY ANALYSIS OF FINGER LAKES RIESLING

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ABSTRACT

As the wine world continues to globalize, and industry competition grows, wine regions have increasingly focused on promoting one or two grape varietals which result in consistently expressive wines that best represent the viticultural area. A variety of studies have concentrated on defining regional cultivar typicity not only to enhance marketing techniques, but also to increase the understanding of a specific cultivar within the region from viticultural, enological, and sensorial perspectives, and findings may be relevant to the entire field. The Finger Lakes region of New York State has put itself on the world wine map through production of Rieslings with definitive sensory character. Preliminary assessments also suggest unique sensory profiles exist in the Rieslings according to which Finger Lake the grapes are cultivated. The sensory properties of Finger Lakes Rieslings, and the presence of subregional character, have not previously been investigated through rigorous, formal sensory analysis. This experiment sought to determine whether Riesling grapes grown along Keuka, Seneca, and Cayuga Lakes and from two distinct clones produced wines with unique sensory and compositional profiles.

Six similar blocks of Riesling were selected to reduce effects of viticultural practices on compositional and sensory outcomes. Two sites, exclusively planted with clone 90 or clone 239, were selected from the east side of each lake. Viticultural treatments were standardized throughout the growing season. Inherent site and seasonal characteristics were recorded, and specific vine physiology and status measurements were collected from each block. Grapes were vinified, in duplicate lots from each site, by a standard winemaking protocol to yield two fermentation replicates. Instrumental analyses (GC-FID and GC-MS) were performed to quantify selected volatile aroma constituents of the Riesling wines. Generic descriptive analysis

(DA) was performed on the wines by eleven panelists, screened for white wine consumption habits and sensory acuity. Sensory reference standards were developed during training and utilized along with intensity standards during orthonasal evaluation of the wines. Wines were also analyzed by HPLC for phenolic acids profiling.

Statistical analyses of the volatile data showed that significant differences existed among some compounds. However, most of these differences were likely of no biological significance based on similarity of overall volatile profiles and vineyard site characteristics such as canopy light environment, vine water status, and crop load, factors which may impact wine quality. Monoterpene and TDN levels were at or below sensory threshold, and linalool was the only compound with apparent correlation to sensory data.

DA panelists established 11 aroma attributes important to Finger Lakes Riesling wines. Wine aroma profiles were similar across vineyard sites, and two-way ANOVA results of lake, clone, and their interaction were not significant. Citrus, pineapple, linalool/floral, melon, and stemmy were among the descriptors present at the highest intensities.

Phenolics data were characteristic of white wines as hydroxycinnamic acids and their tartrate esters dominated the profile. Higher concentrations of fertaric acid than coutaric acid were observed. While ANOVA showed significant results for lake, clone, and their interactions, clone had the strongest effect.

These experiments indicate that sensory and aroma profiles of Riesling wines were similar despite differences in clonal material and growing conditions. However, the importance of seasonal growing conditions should not be overlooked as this experiment should be repeated over multiple years. The Riesling wines were also analyzed with less than six months of bottle age, and aging has the potential to impact

wine differentiation. This sensory and volatile data is among the first to be reported for Riesling in the Finger Lakes. Riesling clone may be of interest to growers and winemakers due to effect on phenolic profile which may impact volatile stability and oxidative browning.

BIOGRAPHICAL SKETCH

Rebecca Erin Nelson was born on August 12, 1984 in Munster, IN to Nancy A. and Richard E. Nelson. She was raised in Schererville, IN with one sister, Nicole. Rebecca attended Lake Central High School and received her diploma in June 2002. She then sought higher education at Purdue University and graduated with a Bachelor of Science degree in Dietetics and Foods & Nutrition in Business in May 2007. Her first exposure to research came when working on an honors project under the guidance of Dr. Mario Ferruzzi in the Department of Food Science. Her work entitled "Synthesis and bioaccessability of Fe-pheophytin derivatives from crude spinach extract" was published in the Journal of Food Science. After graduation, Rebecca completed several internships in the food and beverage industry. She spent eleven weeks in the nutrition applications and regulatory group at Kraft Foods in Chicago, IL followed by a yearlong trainee program at the Nestlé Research Center in Lausanne, Switzerland. At Nestlé, Rebecca worked in the nutrient bioavailability group where she enhanced her analytical chemistry skills specifically related to liquid chromatography-mass spectrometry. With a keen interest in wine, she returned to the USA to complete a harvest internship as a cellar hand at a custom crush facility in Oregon's Willamette Valley in the fall 2008. During this time, she was accepted at Cornell University with the opportunity to work with Dr. Anna Katharine Mansfield in enology. As of January 2009, Rebecca has been investigating sensory and chemical characteristics of Riesling wines in the Finger Lakes region of New York State.

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LITERATURE REVIEW

1.1 Introduction

Riesling is recognized as the flagship wine grape of the Finger Lakes American Viticultural Area (AVA) in New York State due to its high quality potential in the region. The introduction of Riesling and other *Vitis vinifera* grapes was initially met with resistance, however. There was a lot of skepticism about whether the Finger Lakes could produce quality wines from noble European *V. vinifera* grapes such as Riesling, because the region was generally thought to be too cold to grow *V. vinifera* cultivars. Things changed in 1962 when Dr. Konstantin Frank took matters into his own hands and planted the first Riesling vines on Keuka Lake. He proved the skeptics wrong by launching a successful winery based solely on *V. vinifera* grapes, and other vignerons started to follow suit. Although many of the vineyards in New York State, including the Finger Lakes, are still planted to native American varieties such as Concord and Niagara, Riesling has been the steady favorite *V. vinifera* cultivar since its introduction back in the mid-twentieth century. As of 2006, a total of 543 acres were dedicated to Riesling production in the Finger Lakes, which accounted for roughly one-third of the *V. vinifera* plantings in the region. Riesling tonnage nearly doubled in the five-year span from 2001 to 2006 (New York Fruit Tree and Vineyard Survey, www.nass.usda.gov), clearly illustrating the cultivar's rapid rise in popularity within the past decade.

1.2 Growing conditions in the Finger Lakes

The Finger Lakes region is located along the 42nd parallel in the United States; the Great Lakes Region macroclimate tempers the variability and temperature

extremes associated with continental climates (http://www.nysaes.cornell.edu/hort/faculty/pool/continentality/continentality.htm). The Great Lakes, Erie and Ontario, provide moderating effects on temperature and precipitation in upstate New York while the Finger Lakes provide an additional lake effect within the region. The result is warmer winters and cooler summers compared to surrounding areas. Whitesell (2005) compared weather data within the Finger Lakes and found that the NEWA weather station located along Seneca Lake (Valois) recorded higher (+1.2°C) average monthly minimum temperatures and lower (-0.8°C) average monthly maximum temperatures compared to the weather station located outside the lake effect zone (Groveland). Thus, the majority of vineyards in the region are situated along the sloping shores of the larger lakes (Seneca, Cayuga, and Keuka) to take advantage of the lake effect. These lakes rarely freeze in the winter, and they buffer extreme cold winter temperatures through the action of cold air drainage, thus preventing winter injury to grapevines. In the summer, the lakes moderate extreme heat fluxes, allowing for slow, even ripening of grapes. The lake effect also prevents premature budbreak and associated frost injuries to grapevines in the spring, and delays the first frost, extending the growing season in the fall (Robinson 2006). Grapevines need a minimum of 170 frost-free days to adequately ripen a crop, and the Finger Lakes provide suitable conditions for high quality winegrowing (Wolf 2007). Table 1.1 depicts the different features of the lakes most important to viticulture in the region. Generally, lake depth influences the extent of the lake effect, as deeper lakes have more water volume and, ultimately, temperature buffering capacity. While lake surface area has been suggested as a contributing factor to the terroir of the Finger Lakes due to enhanced light exposure to the grapevines (Smith 2009a), this hypothesis has not been investigated.

Table 1.1 Features of the three Finger Lakes of main interest to viticulture

Lake	Mean depth (m)	Surface area (km^2)	Elevation (m)
Keuka	31	47	218
Seneca	89	175	136
Cayuga	55	172	116

A recent in-depth survey by Meinert and Curtin (2005) clearly portrayed the wide range of geology and topographical attributes that are unique to the Finger Lakes. Glaciers carved out the Finger Lakes and left behind sediments from the Pleistocene era. The combination of lakes, soils, topography, climate and their interactions make the Finger Lakes highly suitable for wine grape production. The post-glacial terrain consists of a combination of shale, sandstone, siltstone, and clay-rich limestone giving rise to a diverse range of soils. There are some general soil trends in the Finger Lakes, such as decreasing pH from north to south due to the presence of limestone deposits in the north, but variability is practically the only constant in Finger Lakes soils. Soil diversity has been reported both within and among vineyards in the Finger Lakes (Cavatorta 2005, Martin 2005, Meinert and Curtin 2005). Cavatorta (2005) investigated Riesling vine vigor in a Finger Lakes vineyard as a product of soil disparity and found dramatic differences only 130 meters apart. The well-drained soil gave rise to better fruit compared to the poorly-drained soil. This research not only illustrated the variable characteristics of soil in the Finger Lakes but also the requirement of good drainage for Riesling production. Therefore, the soil diversity may potentially lead to differences in grape and wine quality through the mediation of grapevine water status which has been the focus of many terroir-related studies (Willwerth et al. 2010, Reynolds et al. 2010).

Elevation of the three lakes, a characteristic of topography, may also influence grape growing conditions. In relation to climate, temperatures generally decrease with increasing elevation at a rate of 0.6°C per 100 meters (Robinson 2006). Cayuga Lake

has the lowest elevation, followed by Seneca and Keuka (Table 1.1). Most vineyards are planted on steep hillsides overlooking the lakes, not only to maximize the beneficial lake effect, but also to help provide the vines with good soil water drainage beneficial to Riesling (Robinson 2006). There is a trend in topography that runs north to south within the Finger Lakes; the lakeshores are steepest along the south end and gradually become flatter in the north. The lake effect does not reach as far inland when the slopes are really steep (http://arcserver2.iagt.org/vll/learnmore.aspx).

According to weather data compiled from the Geneva Research Farm located at the north end of Seneca Lake between 1971 and 2000, there were an average of 7 days per year with minimum temperatures below -17°C (http://nowdata.rcc-acis.org/BUF/pubACIS_results); thus, wintery injury is a real concern in the Finger Lakes. However, Riesling is categorized as one of the most cold-hardy *vinifera* varieties because 50 to 100% primary bud kill may not be expected to occur until temperatures reach as low as -20°C to -26°C (Wolf 2007). Riesling is late to break bud in the beginning of the growing season, which is a positive attribute in a region where spring frost is a threat. Even though Riesling gets off to a slow start, it has the ability to continue maturing well into the fall when daily temperatures begin to decline (Wilson 1998). Late season ripening also allows Riesling to be made in a variety of styles ranging from bone dry to dessert. This characteristic is a reflection of the grape's natural acidity and versatility in balancing a range of sugar levels. While Riesling can be grown in warmer climates, it tends to lose its natural acidity and flavor complexity (Robinson 2006). The slow and steady accumulation of heat during the Finger Lakes growing season corresponds to consistent ripening and flavor development of the fruit year after year, which results in "the best expression of terroir" according to van Leeuwen and Seguin (2006).

1.3 American Viticultural Areas in the Finger Lakes

Similar to the controlled appellation systems of the old world, an American Viticultural Area (AVA), defined and approved by the Alcohol and Tobacco Tax and Trade Bureau within the Code of Federal Regulations, encompasses a specific viticultural region with unique growing conditions (Robinson 2006). The Finger Lakes region consists of three AVAs, designated as Finger Lakes, Cayuga Lake, and Seneca Lake. The Finger Lakes AVA was established in 1987 and covers all eleven Finger Lakes from Conesus Lake in the west to Otisco Lake in the east (27 CFR 9.34); the main lakes for grape growing are Cayuga, Seneca, Keuka, and Canandaigua, four of the larger lakes in the region. Cayuga Lake and Seneca Lake AVAs are often referred to as sub-appellations within the Finger Lakes AVA. Cayuga Lake AVA was established in 1988 (27 CFR 9.127), and Seneca Lake AVA followed in 2003 (27 CFR 9.128). These sub-appellations were defined in order to emphasize the distinct growing conditions of the individual lakes. However, wineries choose to use the Finger Lakes AVA on wine labels versus Seneca Lake or Cayuga Lake AVA, most likely due to greater familiarization with the Finger Lakes for marketing purposes outside the region (Meinert and Curtin 2005).

1.4 Finger Lakes Riesling in the popular press

Discussion of Riesling typicity and terroir has infiltrated the media in online publications such as *Appellation America*, *Wines & Vines*, and *New York Cork Report.* The latter source argued that Finger Lakes Riesling not only has a sense of place derived from the perfect union of grape and environment, but that the sensory characteristics are distinct from other world-renowned Riesling terroirs located in Germany and Alsace. Riesling has long been recognized for conveying distinctive sensory attributes dependent on geographic origin, partly due to the fact that

enological practices, which have the potential to mask varietal qualities (i.e. oak aging), are not typical for Riesling production. Smith (2009b) further defined the sensory properties that may be perceived in Finger Lakes Riesling, including but not limited to: fruity notes of apple, pear, citrus, and peach; floral aromas of jasmine, lilac, and honeysuckle; green notes of fresh cut flowers, cucumber, and dill; and aromas of honey, baking spice, and the signature Riesling petrol note. He further claimed that the mouthwatering acidity and elusive minerality flavors contribute to the overall typicity of Finger Lakes Riesling (Smith 2009b). Moreover, informal sensory assessments have generated hypotheses that sub-regional Riesling character exists according to the terroir of Keuka, Seneca, and Cayuga Lakes. The simplified, collective analysis of this phenomenon by Smith (2009a) is that the southeast end of Seneca Lake produces wines with more tropical fruit like pineapple and melon as well as ripe peach aromas. This sub-region has been dubbed the banana belt for its purported warmer climate compared to the rest of the Finger Lakes region. On the other hand, Cayuga and Keuka Lake Rieslings have been characterized by more floral and less fruity aromas based on the distinctive, cooler growing conditions influenced by the topography of the lakes (Smith, 2009a).

1.5 The concept of terroir

According to Vaudour (2002), terroir may refer to the nutrition and quality of grape growing, the definition of territorial boundaries, the advertisement of a particular image, the establishment of an identity or tradition, all of the above, and more. The terroir concept has been highly controversial and thus the topic of several discussions regarding its precise definition and application within the scientific world of wine (van Leeuwen and Seguin 2006, Bohmrich 1996, Vaudour 2002). As terroir was historically based on soil classification used to designate viticultural areas in

France, the majority of terroir studies have placed emphasis on soil composition (Vaudour 2002). However, terroir has evolved to include other factors such as climate, topography, and even viticultural and winemaking practices (Bohmrich 1996). While viticultural and winemaking practices are debatable because they represent human interventions which can be reproduced elsewhere, some terroir studies continue to incorporate these cultural factors into research. Fischer et al. (2009) investigated sensorial attributes of German Rieslings from different geographical classifications produced by standardized and winery-specific vinification methods. They found that wines from the former category were already sensorially distinct, but the individual winemaking protocols intensified the differences. All of the wines were influenced by environmental factors and were expressions of the growing conditions, but perhaps the wines from the standardized winemaking were not as typical of Rieslings being sold on a commercial scale in the respective sub-regions. However, it is impossible and impractical to capture all of the variability introduced by winemaking practices as well as from the environment. Nevertheless, research has focused on elucidating the impact of specific growing conditions on Riesling varietal typicity and the corresponding volatile composition responsible for distinct aroma profiles.

1.6 Wine typicity

Typicity, from the literal translation of the French term typicité, refers to the quality of a wine produced from a designated area (Vaudour 2002, Robinson 2006). The identification of a wine typicity leads to consumer expectation for a consistent sensory experience of wines from a distinct region. Research by Lund et al. (2009) involved descriptive analysis to evaluate Sauvignon blanc sensorially and chemically for aroma constituents as a means for distinguishing New Zealand Sauvignon blanc from other regions where the varietal wine is produced. Additionally, a consumer

study performed as part of this work verified the existence of a preferred regional character. Defining typicity not only serves a critical marketing purpose for attracting and retaining a customer base but also aids in establishing specific quality standards and production guidelines for the wine industry. Research efforts in Canada and Germany have investigated the impact of regional growing conditions on varietal Riesling wines. As a result of those scientific evaluations, Riesling typicity has been defined within those regions (Fischer et al. 1999, Douglas et al. 2001, Fischer et al. 2009).

1.7 Varietal character

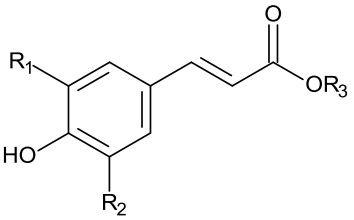
Grapes and musts have relatively little flavor and aroma compared to wine, but numerous organic compounds present in grape berries end up in the wine matrix. While some remain intact, the vast majority become metabolites of the winemaking process (Fischer 2007). Further, it is through alcoholic fermentation, winemaking techniques, and bottle aging that aromas and flavors are developed to characterize specific varietals such as Riesling (Swiegers et al. 2005). More often than not, plant secondary metabolites are the organic compounds being transformed into odor active volatiles and other constituents with major sensory implications. Unlike primary metabolites (i.e. sugars, organic acids) which are involved in vital growth, development, and reproduction processes in grapes, secondary metabolites have been associated with alternative pathways for detoxification, defense against disease and environmental stress, and mechanisms for attracting pollinators and seed dispersal, to name a few (Rhodes 1994, Crozier et al. 2006). Some secondary metabolite classes of significance to wine quality and varietal character include phenolic compounds, terpenoids, and sulfur-containing compounds (Fischer 2007). Some higher alcohols have also been associated with varietal character (Dunlevy et al. 2009). The

combination of these compounds, rather than one individual compound, gives rise to varietal character, although there are some exceptions (Fischer 2007). Determining the specific constituents of wine and their contribution to varietal character in order to completely understand the basis of wine quality continues to be at the forefront of wine research. The following sections will address the classes of compounds of particular interest to Riesling varietal character.

1.7.1 Phenolics. Structurally, phenolics are organic compounds containing one or more benzene rings with at least one hydroxyl group. They are typically categorized into two overarching classes based on their chemical composition: nonflavonoids and flavonoids. The nonflavonoid group can be further divided into phenolic acids and stilbenes; phenolic acids consist of C_6-C_1 benzoates and C_6-C_3 hydroxycinnamates. The subgroups of the C_6-C_3-C_6 flavonoids most important to wine include flavonols, anthocyanins, and flavon-3-ols and their polymers (Crozier et al. 2006, Kennedy et al. 2008).

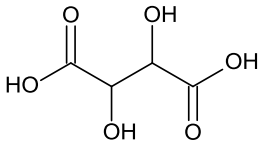
The phenolic makeup of grapes and wine has historically been studied due to its impact on the major organoleptic wine qualities such as taste, color, flavor, and mouthfeel (Kennedy et al. 2006) as well as its association with health benefits (Monagas et al. 2005). While phenolics are more abundant and diverse in red wines, an appreciable amount of research has been aimed at white wine phenolics. Nardini and colleagues (2009) showed that white wine phenolics are bioavailable to humans. Hydroxycinnamic acids, which account for roughly 75% of phenolic species in white wines, and to a lesser extent monomeric catechins and other flavonoids have been investigated for their antioxidant capacity (Baderschneider and Winterhalter 2001, Makris et al. 2003), contribution to must and wine oxidative browning (Antonelli et al. 2010, Boselli et al. 2010, Cheynier et al. 1989, Kilmartin et al. 2007, Recamales et al. 2006, Schneider 1998), and bitterness in white wine (Vérette et al. 1988). The grape-

derived hydroxycinnamic acids are typically found esterified to tartaric acid (Ribéreau-Gayon 1965, Singleton et al. 1978) as shown in Figure 1.1 and are located in the flesh of the grape berry. Other phenolic compounds are extracted from the skins and seeds during grape processing and thus are largely dependent on winemaking protocols (Kennedy 2008).



Hydroxycinnamic acid	R_1	R_2
caffeic	OH	H
p-coumaric	H	H
ferulic	OCH_3	H

R_3 esterification



tartaric acid

Figure 1.1 Chemical structures of hydroxycinnamic acids and tartrate ester derivatives (Symyx Draw, Symyx Solutions, San Diego, CA).

Phenolic concentrations in wines are indisputably altered by viticultural and enological practices throughout the grape growing and winemaking process (Kennedy et al. 2006); nonetheless, investigations have also focused on typifying wine varietals based on phenolic constituents as influenced by genetics and/or geographic origin (Nagel et al. 1979, Soleas et al. 1997, de Villiers et al. 2005, Pour Nikfardjam et al. 2007, Darias-Martín et al. 2008). Concentrations of hydroxycinnamic acids in Riesling wines have been reported in several studies (Goldberg et al. 2000, Soleas et al. 1997, Somers et al. 1987), and Riesling has been the white wine of interest in several studies

on phenolics. Goldberg et al. (2000) evaluated commercial monovarietal wines, including Riesling, in the Finger Lakes Region which provides a foundation for characterizing the Finger Lakes Riesling phenolic profile.

Volatile phenols are derived from hydroxycinnamic acid precursors, and as their name suggests, they contribute to wine aroma. They are not found in grapes but are formed by enzymatic hydrolysis during the winemaking process. Some *S. cerevisiae* yeast strains have enzyme activity to decarboxylate free HCAs into volatile phenol compounds, specifically transforming coumaric and ferulic acid to 4-vinylphenol and 4-vinylguaiacol, respectively, with spice and clove aromas (Chatonnet et al. 1993). Commercial pectinases used in settling musts during the processing of white wine may also contribute to the formation of volatile phenols (Lao et al. 1997, Dugelay et al. 1993). Volatile phenols have been reported above sensory threshold in Riesling wines which infers that their aromas contribute to Riesling varietal character (Sacks et al. 2010).

1.7.2 Terpenoids. All terpenoids are made from the same 5-carbon unit precursors (isoprenes) and thus are classified by their total number of carbon molecules (Jackson 2006). The most important families of terpenoids in the context of grape and wine aroma include C_{10}-monoterpenes, C_{15}-sesquiterpenes, and C_{13}-norisoprenoids. The free forms of these compounds are present in grapes, but the vast majority are bound to sugar moieties, and stored in the berry skins, although the distribution appears to be compound- and cultivar-specific (Swiegers et al. 2005). In glycosylated form, the compounds are non-volatile and do not contribute to grape and wine aroma. However, grape crushing and alcoholic fermentation can metabolize the bound conjugates through the action of β-glycosidase enzymes, rendering free aglycones with aromatic properties. However, this process for enhancing volatile aroma is limited by the must conditions, enzyme-substrate specificity, and subsequent

conversion of aglycones to less aromatic species. Acid hydrolysis also releases precursors into volatile forms and is a major factor in the evolution of wine aroma bottle aging (Lund and Bohlman 2006, Ribéreau-Gayon et al. 2006, Fischer 2007).

The monoterpenes are known for their pleasant, floral-like and fruity aromas, and they are found in a wide range of winegrape cultivars. They are predominately associated with grapes of the Muscat family. However, monoterpenes provide defining characteristics to aromatic white grape varieties such as Riesling and Gewurztraminer. These latter varietals have been classified as non-muscat aromatics based on free monoterpene levels typically in the range of 1-4 µg/L (Strauss et al. 1986). While dozens of monoterpenes have been identified, the major compounds of interest include linalool, citronellol, nerol, geraniol, and *cis*-rose oxide. Due to their comparatively lower detection thresholds in the range of 10-100 µg/L, and their presence as free forms within grapes, these compounds are among the more likely contributors to wine aroma profiles (Strauss et al. 1986, Dunlevy et al. 2009, Ribéreau-Gayon et al. 2006). Monoterpenes exist in forms other than alcohols, such as diols and oxides, but these species are generally less volatile (Ribéreau-Gayon et al. 2006). Because odor active monoterpene levels are dynamic in grapes and wine, analyses typically involve measuring both free and potentially volatile terpenes (Strauss et al. 1986, Reynolds et al. 2007). Research investigating the accumulation and degradation of monoterpenes in grapes has primarily focused on Muscat varieties, and results have indicated that maximum concentrations are reached post-veraison (Strauss et al. 1986). A recent publication by Kalua et al. (2010) monitored geraniol in Riesling from bloom to harvest and found detectable levels shortly after fruit set, but not again until harvest. While no information for other monoterpenes typically found in Riesling was reported in this work, this trend is in line with other findings (Wilson et al. 1984). Environmental factors such as cluster light exposure and water status have been shown

to impact monoterpene levels in non-muscat aromatic grapes and wine (Reynolds et al. 1994, Skinkis et al. 2010, Reynolds et al. 2010, Willwerth et al. 2010). Further, grapes grown in warmer climates tend to have lower monoterpene concentrations overall (Creasy and Creasy 2009). These factors suggest the potential for variation in monoterpene concentrations on a regional basis according to overarching characteristics of terroir, ultimately manifesting as regional cultivar typicity.

C_{13}-norisoprenoids are breakdown products of the C_{40} terpenes, more commonly known as carotenoids, and are structurally divided into two categories based on oxygenation: megastigmanes (oxygenated) and non-megastigmanes. The major megastigmane forms are both ketones, β-ionone and β-damescenone, and they are typically found above sensory thresholds of approximately 50 and 800 ng/L, respectively, in model wine (Ribéreau-Gayon et al. 2006). Their sweet fruit and floral aromas have been claimed to enhance, rather than contribute to, particular varietal character, as they are both ubiquitous in grapes (Dunlevy et al. 2009). Vitispirane is a non-megastigmane with eucalyptus odor qualities, but the most notable non-megastigmane associated with wine aroma is TDN (1,1,6-trimethyl-1,2-dihydronaphtalene) which imparts a distinct petrol or kerosene note typical of aged Riesling. While this compound is not present in grapes, it is formed in wine over time by acid hydrolysis (Fischer 2007). Australian Rieslings were analyzed for a wide range of volatile compounds, including TDN, and the older wines were significantly higher in TDN concentration (Smyth 2005). The reported sensory threshold for Riesling is 20 µg/L (Simpson 1978), but recent research efforts by Acree and colleagues (Sacks et al. 2010) have resolved that this value is overestimated. The results of their forced-choice ascending threshold procedure showed that the recognition threshold is at least two-fold lower in both dilute ethanol and model wine, and the detection threshold is as much as ten orders of magnitude lower than

previously reported. At 2-3 μg/L levels in wine, TDN may not be recognized, but it possibly has other wine-modifying effects, such as fruity aroma suppression. While TDN may add complexity at low concentrations, this attribute is generally undesirable at higher levels in wine. Thus, much research has focused on the origin of TDN in terms of potential precursors (Marais et al. 1992, Winterhalter et al. 1990), the relationship between grape norisoprenoid precursors and wine C_{13}-norisoprenoids (Crupi et al. 2010, Loscos et al. 2007), and viticultural practices and environmental conditions impacting TDN levels (Linsenmeier and Lohnertz 2007, Kwasniewski et al. 2010, Marais et al. 1992). Increased cluster exposure and hot, dry climates have been linked to higher TDN concentrations in wine although these findings have not been entirely consistent (Fischer 2007).

1.7.3 Sulfur-containing compounds. Although sulfur-containing compounds such as 3-mercaptohexanol and 3-mercaptohexyl acetate, with their characteristic grapefruit and passion fruit aromas, have been more commonly associated with varietal aroma of Sauvignon blanc wines (Dubourdieu et al. 2006), these volatiles have also been reported above sensory threshold in Alsatian Rieslings (Tominaga et al. 2000). Limited quantitative data is available for these volatile thiols in Rieslings from other regions. Both compounds are found in the grape as odorless precursors, bound to cysteine or glutathione, and are released during fermentation by the activity of yeast enzymes (Dunlevy et al. 2009). Low vine water and nitrogen status has been correlated with decreased concentrations of volatile thiol conjugates in berries at harvest, and the researchers suggested that this phenomenon may be applied to other white grape cultivars as well (Peyrot de Gachons et al. 2005).

1.7.4 Higher alcohols. Because higher alcohols are formed during the fermentation process (Bell and Henschke 2005), they are not typically associated with varietal character of a particular cultivar. However, Oliveira et al. (2006) reported that

the ratios of C_6 alcohols could differentiate white wines from Portugal and other cultivars. The C_6 alcohols, which have characteristic green aromas, are derived from fatty acid oxidation and the breakdown of amino acids (Dunlevy et al. 2009). Therefore, many studies have investigated the relationship between must nitrogen concentration and C_6 alcohols and other higher alcohols, but further work is necessary to elucidate the processes involved in production of these compounds (Bell and Henschke 2005). A characterization study of Australian Rieslings quantified a range of higher alcohols and their esters, including phenylethanol and phenethyl acetate (Smyth 2005), which have also been found in grape berries and contribute rose and honey aromas (Dunlevy et al. 2009). While these compounds have the potential to differentiate wines by variety, nutrition modifications to musts may have more impact that varietal or origin (Bell and Henschke 2005). Further work is necessary to investigate these hypotheses.

1.8 Clones

Grape species may be classified in many ways, with color (i.e., red vs. white) and name of cultivar (i.e., Riesling) being the most significant from viticultural, enological, and commercial standpoints. While these primary differences greatly contribute to the depth and breadth of the grape and wine industry, diversification may also be achieved through clonal selection at the cultivar level. Clonal selection allows for alteration of a cultivar without the loss of varietal character (Jackson 2008). As of 2000, over eighty Riesling clones were identified and recorded in Germany (Regner et al. 2000), which could all be cultivated, vinified, and marketed as Riesling. The extent to which clones differ is dependent on many factors, such as cultivar susceptibility to mutations and age, as natural variation by mutation occurs slowly over time (Jackson 2008). Comprehensive statistical analysis of thirty Riesling clones from independent

studies in Germany showed that most of the variability in yield, soluble solids, and acidity was due to environmental conditions, and Riesling clones were noted to be much less variable than other cultivars (Laidig et al. 2009). Nevertheless, clonal selection continues to serve as a beneficial tool for vignerons in search of optimizing varietal grape quality through traits such as enhanced disease resistance, aroma profile, or winter hardiness. All of these characteristics contributed to the selection of Riesling clone 90 in the Finger Lakes region of New York State (Cattell 2008). Most Riesling clonal research has been conducted outside of the United States, however, with variable results. Schoeffling (1990) reported no sensory differences in nine Riesling clones from a multi-year investigation in Germany. In contrast, monoterpene profiles were shown to be significantly different among some Riesling clones in South Africa, but no sensory analysis was conducted to assess perceptible sensory difference (Marais and Rapp 1991).

1.9 Viticultural analyses

In viticulture studies, the specific parameters assessing growing conditions have varied due to diverse research questions, different experimental conditions, and the inherent complexity of the field. Regardless, methodologies have involved measuring quantitative variables rather than qualitative growing conditions.

1.9.1 Carbon isotope ratio analysis. Carbon isotope ratio composition has been correlated with predawn leaf water potential and shown to reflect vine water status. Carbon fixation by grapevines is altered under stressful conditions, like drought, such that low soil moisture detected by drying roots triggers leaf stomatal closure resulting in discriminatory utilization of ^{13}C and ^{12}C isotopes. More specifically, the $^{13}C/^{12}C$ ratio increases which can be quantified in leaf and berry tissue as an indicator of water stress (Farquhar et al. 1989, Gaudillere et al. 2002). Specific grades of grapevine water

stress have been previously defined according to $\delta^{13}C$ compositions ranging from severe water deficit (> -21.5‰) to no water deficit (< -26‰) (Van Leeuwen et al. 2008). Leaf water status was suggested as a better indicator of current water status while $\delta^{13}C$ in berries represents average water status for the entire season (Van Leeuwen et al. 2004). Grapevine genotype has also been implicated as a secondary variable affecting $\delta^{13}C$ composition among different grapevine cultivars (Gibberd et al. 2001, Gaudillere et al. 2002).

1.9.2 Enhanced point quadrat analysis. The point quadrat analysis technique was introduced by Smart and Robinson (1991) to assess canopy architecture. Canopy transect data was computed to yield data for canopy gaps, leaf layers, exterior leaves, and exterior clusters. However, this method was modified by Meyers and Vanden Heuvel (2008) to enhanced point quadrat analysis (EPQA) to evaluate biomass and photon flux distribution together in greater detail using the Enhanced Point Quadrat Analysis-Canopy Exposure Mapping Tool Set (Version 1.6.2 Excel 2007) developed by Meyers. The new set of metrics allows for greater precision and application. Some of the specific metrics of interest included occlusion layer number (OLN), cluster exposure level (CEL), leaf exposure flux availability (LEFA), and cluster exposure flux availability (CEFA).

1.9.3 Soil and petiole analyses. Soil and petiole analyses have become routine for assessing site suitability and vine nutrient status, respectively (Wolf 2007). In regional typicity studies, complete soil profiles of physical, chemical, and/or biological soil properties have been performed (Gómez-Míguez et al. 2007, Peyrot des Gachons et al. 2005, Bodin and Morlat 2006, de Andrés-de Prado et al. 2007, Reynolds et al. 2007, Reynolds et al. 2010, Willwerth et al. 2010). The physical properties of soil, or soil texture, have received the most attention. Soil texture is determined by the parent rock material. In contrast to soil chemical and biological

properties which can be altered by soil amendments, soil texture is only changed by the normal weathering of bedrock over time (White 2003). De Andrés-de Prado et al. (2007) studied the impact of soil on phenolic composition and sensory characteristics of Grenache. Detailed soil profiles were obtained for the different experimental plots, and the significant results were related back to specific soil properties such as available water capacity. While petiole analyses may be performed to investigate suspected nutrient deficiencies (Wolf 2007), they have also been used to determine whether specific nutrient concentrations correlate with vine size, yield components, and berry composition (Reynolds et al. 2007).

1.9.4 Climate data collection. Climate data is typically collected via on-site weather stations or from online weather networks such as NEWA. Growing Degree Days (GDD) is the most common metric related to length of the growing season in viticulture and is a measurement of heat summation (Wolf 2007). Several studies have computed GDD from temperature data for application in scientific research (Van Leeuwen et al. 2004, Koundouras et al. 2006). Light conditions have been reported in varying ways such as through measurements of photosynthetically active radiation (PAR) (Sandler et al. 2009) or sunshine hours (Van Leeuwen et al. 2004, Peyrot de Gachons et al. 2005), but this climate component has not received as much attention as temperature and precipitation.

1.9.5 Vine balance assessment. The ultimate goal in viticulture is to balance vegetative growth with fruit production to yield high quality grapes from healthy grapevines. Therefore, a variety of metrics have been developed to assess vine balance and to measure crop yields (Dry et al. 2005). A variety of studies on Riesling have reported yield components and/or crop load (ratio of fruit weight to pruning weight) in attempt to correlate data with vine status or grape/wine quality (Reynolds et al. 1994, Reynolds et al. 2007, Reynolds et al. 2010, Spayd et al. 1993). Some of the metrics

have included average berry weight, average cluster weight, average berries per cluster, average pruning weights, etc. Optimal shoot density for Riesling has been suggested as 16-26 shoots per meter (Reynolds et al. 1994), and the recommendation for crop load is 5-10 (Wolf 2007).

1.10 Sensory analysis

Generic descriptive analysis has become the industry standard for sensory evaluation of wine. Several studies have utilized this method to qualitatively and quantitatively characterize Riesling (Fischer et al. 1999, Douglas et al. 2001, Fischer et al. 2006, Reynolds et al. 2010, Willwerth et al. 2010) and other varietals (Cliff et al. 2002, Chapman et al. 2004, Mirarefi et al. 2004, Kontkanen et al. 2005, de Andrés-de Prado et al. 2007, Cortell et al. 2008, Lund et al. 2009). Despite differences in number of panelists, length of panel training, types of scales, assessment of sensory attributes, etc., the general approach, which involves training a set of panelists to judge a product based on mutually agreed upon sensorial constituents, is fairly standard. The wine aroma wheel (Noble et al. 1987) is often incorporated during the first training phase to inititate generation of descriptors. Advantages of this method include calibration of the selected descriptors using reference standards, and training the panelists on intensity ratings. Descriptive analysis results in the development of a sensory lexicon upon which the wine is evaluated (Lawless and Heymann 1998), and the variation of attribute intensities is paramount to determine if the wines are significantly different (Meilgaard 2007). While it is optimal for the wines to first undergo difference testing for verification that differences do exist, this approach is often impractical. Duo-trio and triangle tests both require large populations for statistical power (Lawless and Heymann 1998), and there is typically a shortage of time and resources (i.e. wine) to carry out both descriptive analysis and difference testing.

1.11 Wine compositional analyses

A wide range of analytical tools are available for the extraction, separation, detection, and quantification of phenolic compounds in wine (Stalikas 2007). The most common method employed for wine phenolics analysis is the Folin-Ciocalteu technique which measures total phenolics. High performance liquid chromatography, alone and coupled to a mass spectrometer, are the popular methods which allow for analysis of individual phenolic compounds (Ebeler 2001). While sample preparation techniques exist (Stalikas 2007), more methods are relying on direct injection of the wine sample following a simple filtration step (Bonerz et al. 2008, Lamuela-Raventos and Waterhouse 1994).

Analysis of wine volatile aroma compounds may also be achieved by chromatography, but gas chromatography (GC) is more common as a means of separation. While higher alcohols and esters may also be quantified by GC, increased sensitivity through mass spectrometry is beneficial for quantification of volatiles at lower concentrations (Ebeler 2001). However, much of the Riesling research on volatile composition has reported grape and wine monoterpenes using a less selective spectrophotometric method for determination of potentially and free volatile terpenes (Reynolds et al. 2007, Skinkis et al. 2008). Since other classes of compounds have been associated with Riesling varietal character, more selective and sensitive means of detection have been employed (Smyth 2005, Tominaga et al. 2000).

1.12 Research objectives

This research sought to characterize Finger Lakes Riesling according to sensory and chemical components and to determine if Riesling produced from Keuka, Seneca, and Cayuga Lakes and from two distinct clones could be distinguished by descriptive analysis with a sensory panel of white wine consumers. By collecting data

related to growing conditions, potential differences in the wine could be analyzed against specific growing conditions along each lake. Additionally, quantitative analysis of the experimental wines based on the descriptor set of sensory attributes would further enhance the understanding of wine character within the region according to Keuka, Seneca, and Cayuga Lakes. Formation of this standardized sensory tool would pave the way for future studies comparing Finger Lakes Riesling to those from other regions. In order for Finger Lakes Riesling to be evaluated alongside Riesling from other signature production areas in the world such as Canada, Germany, and Australia, there was a need to first define its typicity within the region. Doing so would enhance consumer understanding of these wines based on key sensory attributes, and industry members could opt to reproduce those characteristics through vineyard site selection and viticultural and enological practices. Since the sensory characteristics of wine as perceived by consumers directly impacts wine purchasing and consumption habits, these efforts would ultimately enhance the marketing and positioning of Riesling from within the region to consumers in the global marketplace.

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CHAPTER 2

THE IMPACT OF LAKE SITE AND CLONE TYPE ON AROMA PROFILES AND CHEMICAL COMPOSITIONS OF RIESLINGS PRODUCED FROM KEUKA, SENECA, AND CAYUGA LAKE VINEYARDS

2.1 Introduction

Riesling's long history and high quality potential in the New York Finger Lakes has led to its recognition as the flagship wine grape in the region. The region's glacial history resulted in diverse soils and temperature- and precipitation-moderating lake effects (Meinert and Curtin 2005), environmental conditions proven compatible with quality Riesling production within the Finger Lakes AVA. A majority of Riesling vineyards in the Finger Lakes are planted along the sloping shores of Keuka Lake, and on its two sub-appellations, Seneca Lake and Cayuga Lake. It is generally accepted that monovarietal Finger Lakes Riesling wines exhibit regional typicity, but the existence of subregional character continues to be a topic of discussion and evaluation. Informal sensory assessments of Riesling wines, some reported in media outlets, have debated sensory differences based on Keuka, Seneca, and Cayuga Lake mesoclimates and growing conditions (Patterson 2006, Smith 2009, Sullivan 2009, Thompson 2009). However, the lack of blind tastings, incongruence in sensory characterization, and a lack of clear ties to viticultural data have limited the usefulness of these evaluations for defining Riesling within the region.

Previous studies suggest that Riesling wines convey distinctive sensory attributes dependent on geographic origin (Douglas et al. 2001, Fischer et al. 2009), as enological practices which have the potential to mask varietal qualities (i.e. oak aging) are not typical in Riesling production. Thus, unique Riesling flavors have been associated with vineyard site differences related to soil, climate, and topography.

Recent research efforts in Canada and Germany have investigated the regional effects on Riesling wines, establishing a foundation for Riesling typicity within those regions (Fischer et al. 1999, Douglas et al. 2001).

Understanding the causes of regionally-specific Riesling characteristics has also been at the forefront of viticulture and enology research, as this knowledge would allow vintners and winemakers to manipulate practices to achieve specific stylistic outcomes. Ongoing research in Ontario vineyards has investigated the effects of factors such as soil and petiole composition, vine vigor, vine water status, and yield components, linking them to Riesling sensory and compositional outcomes (Reynolds et al. 2007, Reynolds et al. 2010, Willwerth et al. 2010). Fischer et al. (2009) explored the role of vineyard designations and bedrock type in German wine regions and compared the effects of commercial vinifications on Riesling sensory profiles. Related research has been performed in a range of other cultivars in France (van Leeuwen et al. 2004), Spain (Gomez-Miguez et al. 2006, de Andres-de Prado et al. 2007), Greece (Koundouras et al. 2006), and South Africa (Marais et al. 1999).

Wine sensory properties are paramount in defining regional wine typicity, and descriptive analysis (DA) has become the industry standard for sensory evaluation of wine. This method has been used in several studies to qualitatively and quantitatively characterize Riesling (Fischer et al. 1999, Douglas et al. 2001, Fischer et al. 2009) and other varietals (Cliff et al. 2002, Chapman et al. 2004, Mirarefi et al. 2004, Kontkanen et al. 2005, Schlosser et al. 2005, de Andres-de Prado et al. 2007, Cortell et al. 2008, Lund et al. 2009). The variation of attribute intensities is paramount in determining significant differences among wines (Meilgaard 2007), and conducting descriptive analysis also contributes to the development of a sensory lexicon (Lawless and Heymann 1998) for varietal wines.

Determining the chemical constituents of Riesling varietal character may enhance understanding of the corresponding sensory profiles. Monoterpenes, C_{13} norisoprenoids, volatile thiols, and volatile phenols are among the aromatic compounds which have been noted to contribute to Riesling varietal typicity (Sacks et al. 2010). Researchers have investigated the impact of growing parameters, viticultural practices, and enological conditions on a variety of these compounds in Riesling (Reynolds et al. 1994, Reynolds et al. 2007, Kwasniewski et al. 2010, Skinkis et al. 2010, Kozina et al. 2008, Marais et al. 1992). Others have focused on characterizing Riesling by aroma compounds. Smyth (2005) conducted sensory and compositional analysis on Australian Rieslings and used multivariate analyses to explore the relationships between data sets. Marais and Rapp (1991) attempted to differentiate Riesling clones by monoterpene composition and found no differences, while acknowledging that these results may not apply to other regions. Along the same lines, phenolic acid profiling has been investigated as a chemotaxonomic approach to differentiating among white grape cultivars and/or region of production (Soleas et al. 1997, de Villiers et al. 2005, Pour Nikfardjam et al. 2007, Goldberg et al. 2000). Additionally, phenolic acids may impact the organoleptic qualities of Riesling (Kennedy et al. 2006), and have been associated with health benefits (Monagas et al. 2005).

The objectives of this study were two-fold: to investigate the environmental factors and growing conditions of Finger Lakes Riesling vineyards, and to characterize Finger Lakes Riesling through sensory analysis, volatile composition, and phenolic acid profiling. This work is designed to test the hypothesis that Riesling wines are sensorially and chemically distinct when produced from fruit grown along Keuka, Seneca, or Cayuga Lakes, as well as from distinct clonal material. To that end, a controlled study with standardized viticultural practices and wine production,

chemical analyses, and detailed sensory evaluation of Riesling was performed to scientifically substantiate claims regarding subregional character based on lake mesoclimate in the Finger Lakes. This exploratory study will ultimately contribute to a greater understanding of the viticultural and enological factors which drive Finger Lakes Riesling typicity. Defining typicity not only serves a critical marketing purpose for attracting and retaining a customer base, but also allows Finger Lakes Riesling to be evaluated alongside Riesling from other signature production areas in the world such as Germany, Canada, and Australia. Such work will enhance consumer understanding of these wines based on key sensory attributes, and will allow industry members to reproduce selected characteristics through vineyard site selection and viticultural and enological practices.

2.2 Materials and Methods

2.2.1 Vineyard site selection. Vineyard sites were chosen on Keuka, Seneca, and Cayuga lakes to represent the major lake mesoclimates in the Finger Lakes American Viticultural Area (AVA). Sites were limited to the east coast of each lake to standardize aspect. Each lake variable consists of one vineyard site with Riesling clone 90 and one with Riesling clone 239; all vines were grafted to rootstock 3309. Vine rows were planted in a north-to-south orientation, and vertical shoot positioning was the standard canopy management system. Though consistency of vine spacing, vine age, and training system was sought, the use of existing vineyards resulted in some site variation. Table 2.1 comprises the inherent characteristics for each Riesling planting used. Vineyard sites were referenced by their respective lake association and clone type (i.e., Keuka 90 or abbreviated K90) as shown. Approximately ten contiguous panels of vines were included in the study at each site.

Table 2.1 Vineyard site characteristics of selected Riesling grapevines

	Vineyard					
Lake	Keuka	Keuka	Seneca	Seneca	Cayuga	Cayuga
Clone	90	239	90	239	90	239
Geographic Location[a]	42.62, -77.07	42.60, -77.07	42.57, -76.86	42.50, -76.88	42.57, -76.59	42.64, -76.64
Vine Age (yrs)	25	7	4	5	3	26
Training (Pruning) System	Double guyot (cane)	Double guyot (cane)	Single guyot (cane)	Single guyot (cane)	Double guyot (cane)	Pendelbogen (cane)
Fruiting Wire Height (m)	0.91, 0.91	0.61, 0.86	0.86, 1.0	1.0	0.61, 0.71	0.86
Vine Spacing (m)	1.8	1.8	1.8	1.8	1.2	1.2
Slope (%)[b]	11.59	12.01	7.18	10.67	8.91	6.15
Elevation (m)[b]	263	266	267	199	197	226
Aspect [b]	Northwest	West	West	West	Southwest	Southwest
Budbreak	May 11	May 11	May 11	May 11	May 11	May 11
Bloom[c]	June 21	June 21	June 21	June 21	June 23	June 23
Veraison[d]	Aug 24	Aug 31	Aug 24	Aug 24	Aug 25	Aug 27
Harvest Date[e]	Oct 22	Oct 13	Oct 21	Sep 30	Oct 6	Oct 21

[a]Latitude and longitude coordinates of experimental plots.
[b]Data sourced from New York Vineyard Site Evaluation System website (www.nyvineyardsite.org) using latitude and longitude coordinates.
[c]Defined by 50% flowering.
[d]Defined by 50% berry softening.
[e]Fruit was harvested at approximately 21 Brix.

2.2.2 Viticultural standardization. To minimize confounding effects from viticultural management practices, shoots were thinned to sixteen shoots per linear meter of row prior to bloom. Three weeks post-bloom, clusters were thinned to two clusters per shoot. Vines at all sites were hedged approximately 1m from actively growing shoot tips at five weeks post-bloom. Disease management and fertilization strategies were executed according to standard practices in viticulture (Wolf 2007).

2.2.3 Viticultural data collection. HOBO Micro Station data loggers (Onset Computer Corporation, Bourne, MA) equipped with photosynthetically active radiation (PAR), temperature, and rain smart sensors were installed at each vineyard site within 50 meters of the panels used in the study. The only exception was the weather station at Seneca 90, situated approximately 500 meters away. Due to inconsistencies in data collection for rainfall, precipitation data were sourced from weather stations (Himrod, Valois, and Lansing for Keuka, Seneca, and Cayuga Lakes, respectively) affiliated with the Network for Environment and Weather Applications website (http://newa.cornell.edu/). Additionally, temperature data were collected from these websites for the initial ten days post-budbreak as the weather stations had yet to be installed at both Keuka Lake sites and Cayuga 239. Average, maximum, and minimum daily temperatures were computed for determining growing degree days (GDD), base 10^{o}C, from data collected at three minute intervals or less from budbreak through harvest according to the dates listed in Table 2.1. Average daily PAR and total daily rainfall were calculated from the raw data. All data were summed across the entire season, and grouped according to the following phenological stages: budbreak to bloom, bloom to veraison, veraison to harvest, and budbreak to harvest.

Soil samples were collected in late May/early June to assess soil health at each location. The sampling protocol followed the procedure described in the Cornell Soil Health Assessment Training Manual (Gugino et al. 2007) with the exception that soil

was collected using a soil corer with dimensions of 15.24 cm x 1.905 cm (length x diameter). Approximately 65 cores total were collected from both sides of the herbicide strip to a depth of 15.24 cm within the experimental panels and mixed thoroughly in a bucket. Two blended samples of 1.4 liters from each vineyard site were submitted for analysis. In addition to the standard tests of physical (aggregate stability, available water capacity, surface hardness, subsurface hardness), biological (organic matter, active carbon, potentially mineralizable nitrogen, root health rating), and chemical (pH, extractable phosphorus, extractable potassium, minor elements) indicators, cation exchange capacity was determined. Analyses were performed as described in the manual (Gugino et al. 2007).

Petioles were collected at bloom from each vineyard site in order to assess vine nutrient status. One or two petioles directly opposite basal flower clusters were selected from each vine. The leaves were immediately removed and discarded; the petioles were washed in a dilute detergent solution, rinsed in distilled water, and allowed to dry out at room temperature until crisp. Two samples of approximately thirty petioles from each vineyard were submitted to the Cornell Nutrient Analysis Laboratory (Ithaca, NY) for testing using established methods for plant tissue analysis (Kalra 1998). Experimental nutrient values were compared to reference standards reported in the Wine Grape Production Guide for Eastern North America (Wolf 2007).

Carbon isotope ratio analysis ($\delta^{13}C$) was performed on leaves and berries from each site to assess vine water stress at veraison and pre-harvest (Farquhar et al. 1989, Gaudillere et al. 2002). At each site, one leaf sample was collected per vine from the sixth leaf position up from the basal end of the shoot. Leaves were oven-dried for 48 hours, pooled together, homogenized, and ground using a coffee grinder (model IDS77, Mr. Coffee, Shelton, CT). Ten berries were randomly selected per vine, stored on ice during transit, and then frozen with liquid nitrogen and stored at -40^{o}C until

further processing. Berries were partially thawed and processed in a food processer (model FSSB100A, Farberware, Needham, MA), aliquotted into vials and ground with model 2000 Geno/Grinder (SPEX SamplePrep, Metuchen, NJ) for 2 minutes at 1400 strokes per minute, and freeze-dried in bulk using Max Series 53 Freeze Dryer (Millrock Technology, Kingston, NY). Approximately 6 mg of dried ground leaf and berry samples for each site from veraison and preharvest were submitted, in duplicate, to the Cornell University Stable Isotope Laboratory in Ithaca, NY for analysis by isotope ratio mass spectrometry using a Delta V isotope ratio mass spectrometer interfaced to a NC2500 elemental analyzer (Thermo Scientific, West Palm Beach, FL). Carbon isotope composition was expressed as $\delta^{13}C = [(R_s - R_b) / R_b] \times 1000$, where $R_s = {}^{13}C/{}^{12}C$ ratio of the sample and $R_b = {}^{13}C/{}^{12}C$ ratio of the Pee Dee Belemnite standard.

Canopy biomass and photon flux distribution were assessed at each vineyard site at veraison by enhanced point quadrat analysis (EPQA) (Meyers and Vanden Heuvel 2008). EPQA was performed by inserting a dowel rod every 20 cm along the east side of the canopy. An AccuPAR LP-80 hand-held ceptometer (Decagon Devices, Pullman, WA) was used to take measurements of photosynthetic photon flux (PPF) between the hours of 10am and 2pm on clear, sunny days. The average of ten readings at fruiting wire height was recorded for every vine. The data was processed by the Enhanced Point Quadrat Analysis-Canopy Exposure Mapping Tool Set (Version 1.6.2 Excel 2007) developed by J. Meyers. The specific metrics of interest included occlusion layer number (OLN), cluster exposure level (CEL), leaf exposure flux availability (LEFA), and cluster exposure flux availability (CEFA).

2.2.4 Harvest and yield components. Fruit maturity was assessed pre-harvest starting mid-September on 100-count berry samples collected weekly from each site by measuring soluble solids with a hand-held digital refractometer model 300016

(Sper Scientific, Scottsdale, AZ), and pH and titratable acidity, expressed as tartaric acid, using a Metrohm 848 Titrino Plus Autotitrator (Riverview, FL). Juice samples (5 mL) were titrated with 0.1N of NaOH (Metrohm) to an endpoint pH of 8.2. Grapes were deemed ready to harvest upon reaching approximately 21°Brix. One day prior to harvest, 100 berries were collected randomly from each panel, in duplicate, to obtain average berry weight. Fruit was harvested between September 30th and October 22nd (Table 2.1). Clusters were hand-picked into individual plastic bags, and cluster counts and fruit weights were recorded by vine. Average cluster weights were computed for each site. Fruit was transported in grape lugs to the Cornell Vinification & Brewing Laboratory in Geneva, NY. Vines were winter pruned according to grower specifications, and pruning weights were obtained on a per vine basis. Seneca 239 pruning weights could not be obtained, but estimates were made based on balanced pruning of one cane per 0.45 kg of pruning weight per vine. Crop load was calculated as the ratio of fruit to pruning weight.

2.2.5 Vinification. Grapes from the six vineyard sites were processed according to a standardized winemaking procedure to minimize the effects of enological parameters on wine characteristics. Fruit from each vineyard was divided at the crush pad and processed to yield duplicate 19 L fermentation lots. The grapes were crushed/destemmed, pressed, transferred to glass carboys, treated with Lallzyme C pectinase (0.02 g/L) (Lallemand, Scott Laboratories, Petaluma, CA) and SO_2 (50 mg/L), and allowed to settle for 24 hours at 18°C. After settling, the juice was racked and adjusted to 22 Brix with sucrose additions prior to inoculation with Lalvin R-HST (0.26 g/L) and Go-Ferm® (0.15 g/L) (Lallemand). Fermaid K (0.125 g/L) (Lallemand) was added 24 hours post-inoculation and at one-third sugar depletion as determined by hydrometer. Diammonium phosphate (Presque Isle Wine Cellars, North East, PA) was added 24 hours post-inoculation to achieve yeast assimilable nitrogen

concentration of 225 mg/L if not inherently met in the must. Fermentations were carried out at 15°C and warmed to 20°C when residual sugar (RS) levels dropped below 30 g/L. The fermentations were racked at RS levels of less than 8 g/L, and SO_2 (40 mg/L) was added. Seneca 90 replicate fermentations stuck at 13 g/L of RS, presumably due to an imbalance in glucose to fructose ratio. Glucose (7 g/L) was added and both replicates were reinoculated with the original yeast strain (0.5 g/L), and fortified with Go-Ferm® (0.625 g/L), to force fermentations to completion. Wines were cold stabilized at 2°C for two weeks minimum, and an additional 50 mg/L of SO_2 was added. Acids were adjusted by addition of potassium carbonate (J.T. Baker, Phillipsburg, NJ) to a target titratable acidity of 10 g/L. Finished wines were bottled in 750 mL glass bottles with corks, and stored at 2°C until further analysis.

2.2.6 Chemical analyses. Following crushing/destemming and pressing, juice samples were immediately collected from each lot for chemical analyses. All analyses were completed in duplicate. Soluble solids, titratable acidity, and pH were determined in juice and wine using the aforementioned methods. A Chemwell 2910 multianalyzer powered by Software Version 6.3 (Awareness Technology, Palm City, FL) was utilized for wine RS and juice YAN determination by enzymatic analyses (Unitech Scientific, Hawaiian Gardens, CA). Free and total SO_2 were measured prior to bottling by FIAstar™ 5000 System (Foss, Eden Prairie, MN). Ethanol analysis was performed using gas chromatography with flame ionization detection (Hewlett Packard GS 5890 Series II, GMI Inc., Ramsey, MN) equipped with FactorFour^{TM} VF-WAXms column, 30 m x 0.25 mm x 1.0 μm (Varian, Inc., Palo Alto, CA). The method was adapted from the AOAC gas chromatographic method for ethanol in wines (AOAC Official Method 983.13). The internal standard was changed to 1-butanol (ACS grade, Sigma-Aldrich, St. Louis, MO), and ethanol was quantified using 10% ethanol standards (v/v) (Sigma-Aldrich).

2.2.7 Organic and phenolic acids by high performance liquid chromatography (HPLC).

A Hewlett Packard 1100 Series HPLC system (Palo Alto, CA), consisting of G1322A degasser, G1312A binary pump, G1313A autosampler, G1316A thermostatted column compartment, and G1315A diode array detector, was used for analysis. Data collection and processing was conducted with ChemStation software version B.04.02 pack 1 (Hewlett Packard, Agilent Technologies, Santa Clara, CA).

Organic acids were quantified in wine using a method adapted from Castellari et al. (2000). Chromatographic separation was achieved with an Aminex HPX-87H column (300 × 7.8 mm) and guard column (30 × 4.6 mm) of the same material (Bio-Rad Laboratories, Hercules, CA). Isocratic elution consisted of 0.045 N sulfuric acid (ACS grade, Sigma-Aldrich) in 6% acetonitrile (99.9% HPLC grade, Acros Organics, Morris Plains, NJ), the flow rate was 0.5 mL/min, and the column temperature was 30°C. All samples were directly injected following syringe filtration through 0.2 μm regenerated cellulose membranes (Corning Inc., Corning, NY). Calibration curves were established using glacial acetic (99.8%, Sigma-Aldrich), and citric monohydrate (Sigma-Aldrich), lactic (85%, J.T. Baker, Phillipsburg, NJ), malic (97%, Alfa Aesar, Ward Hill, MA), and tartaric (99.5%, Sigma-Aldrich) acid standards over appropriate ranges typically observed in wine, and wines were analyzed in duplicate. Quantification was determined by peak areas at 280 nm.

Phenolic acids were measured in wine using a method adapted from Bonerz et al. (2008). Chromatographic separation was achieved with a ChromSep (LiChrospher) RP-18 endcapped column (250 x 4.6 mm, 5 μm) (Varian, Palo Alto, CA) and guard column of the same stationary phase. Gradient elution was carried out with water/phosphoric acid (99.5/0.5, v/v) and acetonitrile/water/phosphoric acid (50/49.5/0.5, v/v). All samples were directly injected (50 μL) following syringe

filtration through 0.2 μm regenerated cellulose membranes (Corning Inc., Corning, NY). Quantification was based on standard calibration curves using gallic acid, (+)-catechin, and (-)-epicatechin at 280 nm and caffeic acid, coumaric acid, and ferulic acid at 320 nm. All standards were purchased from Sigma-Aldrich. HCA tartrate esters (caftaric, coutaric, and fertaric acids) were identified according to retention times and reference absorption spectra previously reported in the literature and quantified based on peak areas of their corresponding free acids. Wines were analyzed in duplicate.

2.2.8 Sensory analysis. Wine consumers who drink white wine a minimum of 1-3 times per month were recruited from Geneva, NY to serve as sensory panelists. All potential panelists passed a sensory acuity test to determine their abilities to distinguish between a 2008 unoaked Chardonnay (Glenora Wine Cellars, Dundee, NY) and a 2008 dry Riesling (Anthony Road Wine Co., Penn Yan, NY), selected by the Cornell Enology Extension Lab for their unique aroma profiles. To serve on the panel, potential panelists had to correctly identify the odd sample in at least three of five triangle tests. The triangle tests were presented to participants in individual sensory booths with red lighting, and the serving orders were randomized within and across participants. Samples consisted of 30 mL of wine at room temperature in standard ISO tasting glasses with petri dish lids and labeled with three-digit random numbers.

Eleven panelists (six male and five female, ages 26 to 56) were included in the study and completed 1-hr descriptive analysis training sessions on a weekly basis for five consecutive weeks. During the first session, panelists were presented with the six wines representing all vineyard sites. Using the wine aroma wheel (Noble et al. 1987) as a reference, they individually generated aroma descriptors to characterize each wine by orthonasal evaluation. Next, with direction from the panel leader, panelists

collectively narrowed the list to eleven terms (Table 2.2). In the subsequent three sessions, panelists developed and familiarized themselves with sensory reference standards to represent each aroma descriptor. Formulas were adapted from the wine aroma wheel when possible. In a final session, panelists underwent intensity training based on the 12-point butanol scale of odor intensity (ASTM 2004). Intensity standards were prepared volumetrically according to the established protocol using 1-butanol (99%, Acros Organics); panelists were presented with a series of 30 mL screw-cap vials containing 12 mL of solution each. Intensity training continued until panelists were able to match unknown intensities to the proper reference values with an average standard deviation of $^{+}$/- 1 from the true intensity.

Table 2.2 Aroma descriptors and corresponding standard reference formulas generated by descriptive analysis

Descriptor	Standard Formulation[a]
pineapple	100 mL canned pineapple juice
melon	100 g cantaloupe, cut into cubes
raspberry	10 frozen raspberries, crushed
dried fruit	equal weight raisins, apricots, prunes (not in wine)
citrus	100 mL grapefruit juice, freshly squeezed
linalool/floral	10 mg/L linalool
clove	5 whole cloves soaked for 1 hour and removed
caramelized	brown sugar (not in wine)
earthy	100 mL water from reconstituted dried portobello mushrooms, 30 min (not in wine)
stemmy	5 g Red Globe grape rachises, crushed
petrol	80 µg/L 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN)

[a]Ingredients were added to 500mL Almaden Golden Chablis (Madera, CA) unless otherwise noted.

During four independent sessions, panelists were presented with the twelve experimental wines in duplicate; six wines were evaluated per session. Wines were randomized across panelists. Sixty mL wine samples, coded with three-digit random numbers, were served in two flights at room temperature in ISO tasting glasses covered with petri dishes. All panelists were given a complete set of sensory standards

and an abbreviated set of butanol intensity standards (points 3, 6, 9, 12) in their individual booths to reference as needed. Panelists were instructed to rate the aroma intensity of each sensory attribute using a 12 cm line scale with gradations corresponding to specific intensities along the butanol scale. Scores were evaluated by measuring the distance, in centimeters, from the left end of the line scale to the mark made by the panelist.

2.2.9 Aroma chemistry analysis. Using a method adapted from Lopez et al. (2002), sample preparation consisted of a solid-phase extraction step in which LiChrolut® EN column (Merck Chemicals, Gibbstown, NJ) was conditioned with 4 mL of dichloromethane (DCM), 4 mL of methanol, and 4 mL of model wine (Danilewicz 2007) prepared with 200 proof ethanol and tartaric acid. All SPE chemicals were supplied by Fisher-Scientific. After conditioning, 50 mL of wine spiked with internal standards was loaded onto the column at a rate of 2 mL/min and then dried by nitrogen for 25 minutes. Elution was carried out with 1.3 mL of DCM, and the eluant was dried to 300 μL under a stream of nitrogen. Wine samples were extracted in duplicate, and extracts were stored at -40°C until analysis. Calibration curves were also prepared, in duplicate, using the same protocol, but aroma standards and internal standards were spiked into model wine. Aroma standards, quantification methods, and calibration ranges are listed in Table 2.3. TDN was synthesized as previously described (Kwasniewski et al. 2010).

Table 2.3 Aroma standards, quantification methods and parameters, and perception thresholds

Compounds	Odorant description	Commercial source	Purity (%)	Quanti-fication Method	Quantification ion(s) (*m/z*)	Calibration Range	Odor Threshold
Acids[a]							
Hexanoic acid	sweat[c]	Aldrich	99.5	FID		0.13-8.2	3[e]
Isovaleric acid	sweat, rancid[c]	Aldrich	99	FID		0.1-9.4	3[e]
Octanoic acid	sweat, cheese[c]	Aldrich	98	FID		0.14-8.8	0.5[f]
Esters[a]							
Diethyl succinate	fruit, wine[c]	Aldrich	99+	FID		0.03-1.9	1.2[d]
Ethyl hexanoate	fruit, apple peel[c]	Acros Organics	99	FID		0.04-2.8	5[e]
Ethyl lactate	fruit[c]	Acros Organics	95	FID		3.8-248	150[d]
Hexyl acetate	fruit, herb[c]	Aldrich	99	FID		0.04-0.7	1.5[f]
Isoamyl acetate	banana[c]	Aldrich	98	FID		0.07-4.4	0.03[e]
β-Phenethyl acetate	rose, honey[c]	Acros Organics	98+	FID		0.09-0.7	0.25[e]
Alcohols[a]							
1-Butanol	medicinal[d]	Acros Organics	99	FID		3.4-218	150[f]
1-Hexanol	herbaceous, grass[d]	Fluka (Sigma–Aldrich)	99	FID		0.3-23	8[f]
2-Phenylethanol	honey, rose, spice[c]	Aldrich	99+	FID		1.1-71	10[e]
Benzyl alcohol	sweet, flower[c]	Acros Organics	99+	FID		0.016-0.99	200[f]
cis-3-Hexenol	grass[c]	SAFC Supply Solution	98	FID		0.01-0.7	0.4[e]
Isoamyl alcohol	burnt[c]	SAFC Supply Solution	98.5	FID		3.8-242	30[e]
Isobutanol	wine, solvent[c]	SAFC Supply Solution	99	FID		3.7-235	40[f]
Methionol	potato, sweet[c]	Aldrich	98	FID		0.04-3	1.2[g]
Volatile phenols[b]							
4-Vinylguaiacol	clove[c]	SAFC Supply Solution	98	GC-MS	135+150	14-853	40[h]
4-Vinylphenol	almond shell[c]	SAFC Supply Solution	10	GC-MS	120	17-1032	180[h]
Terpenes[b]							
cis-Rose oxide	flower[c]	Fluka (Sigma–Aldrich)	10	GC-MS	69+139	0.3-18	0.2[e]
Citronellol	rose[c]	Aldrich	95	GC-MS	67	2.3-36	100[h]
Geraniol	rose[c]	Acros Organics	99	GC-MS/MS	123	2.6-41	30[e]
Linalool	flower[c]	SAFC Supply Solution	97	GC-MS	69+121	2.4-37	15[e]
Nerol	flower[c]	Aldrich	99	GC-MS	69	2.5-39	400[g]
Norisoprenoids[b]							
TDN	petrol[g]	In-house synthesis	99+	GC-MS	142+157+172	0.5-28	20[i]
β-Damascenone	honey, apple, rose[c]	SAFC Supply Solution	1.1-1.3wt	GC-MS	69+121	0.3-20	0.05[h]
Internal Standards[b]							
2-Ethyl 3-dodecanol		Aldrich		GC-MS	185	899	
2-Octanol		Sigma	97	GC-MS	45	288	
2-Secbutylphenol		Aldrich	98	GC-MS	121	387	

[a,b]Values listed in mg/L and µg/L, respectively.
[c, d, e, f, g, h,i] Correspond to references www.flavornet.org, Peinado et al. (2004), Guth et al. (1997), Aznar et al. (2003), Ribereau-Gayon et al. (2006), Lopez et al. (2002), and Simpson et al. (1978), respectively.

Wine and calibration curve extracts were analyzed by GC-MS using a Varian CP-3800 gas chromatograph coupled to a Varian Saturn 2000 ion trap MS (Walnut Creek, CA) with a 25-220 m/z mass range. Separation was performed on a Varian VF-Wax MS column (30 m x 0.25 mm x 0.25 μm) with Varian deactivated precolumn (10 m x 0.25 mm). The carrier gas was helium at a constant flow rate of 1 mL/min. The temperature program was 40°C for 8 min, raised to 170°C at 5°C/min, raised to 250°C at 10°C/min, and held for 3 min. The transfer line, manifold, and ion trap temperatures were 250°C, 50°C, and 170°C, respectively. One μL of sample was injected splitless using a Varian PTV 1079 injector at 250°C. Data collection and processing was performed with Saturn GC/MS Workstation version 5.52 (Varian Inc., Palo Alto, CA). Quantification ions are listed in Table 2.3. Quantification was determined by the peak area ratio of the compound of interest to the corresponding internal standard. The internal standards 2-octanol, sec-butylphenol, and 3-ethyl 3-dodecanol were used for quantifying monoterpenes, volatile phenols, and C13 norisoprenoids, respectively.

Wine and calibration curve extracts were analyzed by GC-FID using a method previously described by Sun et al. (2011). GC-FID analyses were performed in duplicate on a CP-3800 gas chromatograph (Varian Inc., Walnut Creek, CA, USA) equipped with a split/splitless injector and a CP-Wax 58 FFAP fused capillary column (30 m × 0.32 mm i.d. x 1.2 μm). Samples (1 μL) were injected in splitless mode with a purge time of 0.75 min. The carrier gas was helium at a constant flow rate of 3 mL/min. The injector and FID detector temperatures were 250 °C and 300 °C, respectively. The temperature program was 55 °C for 5 min, raised to 163 °C at 3 °C/min, raised to 250 °C at 10 °C/min, and held at 250 °C for 15 min. Galaxie Workstation v.1.9.3.2 (Varian, Inc. Walnut Creek, CA, USA) was used for data acquisition and analysis. Quantification for all compounds was determined by the peak

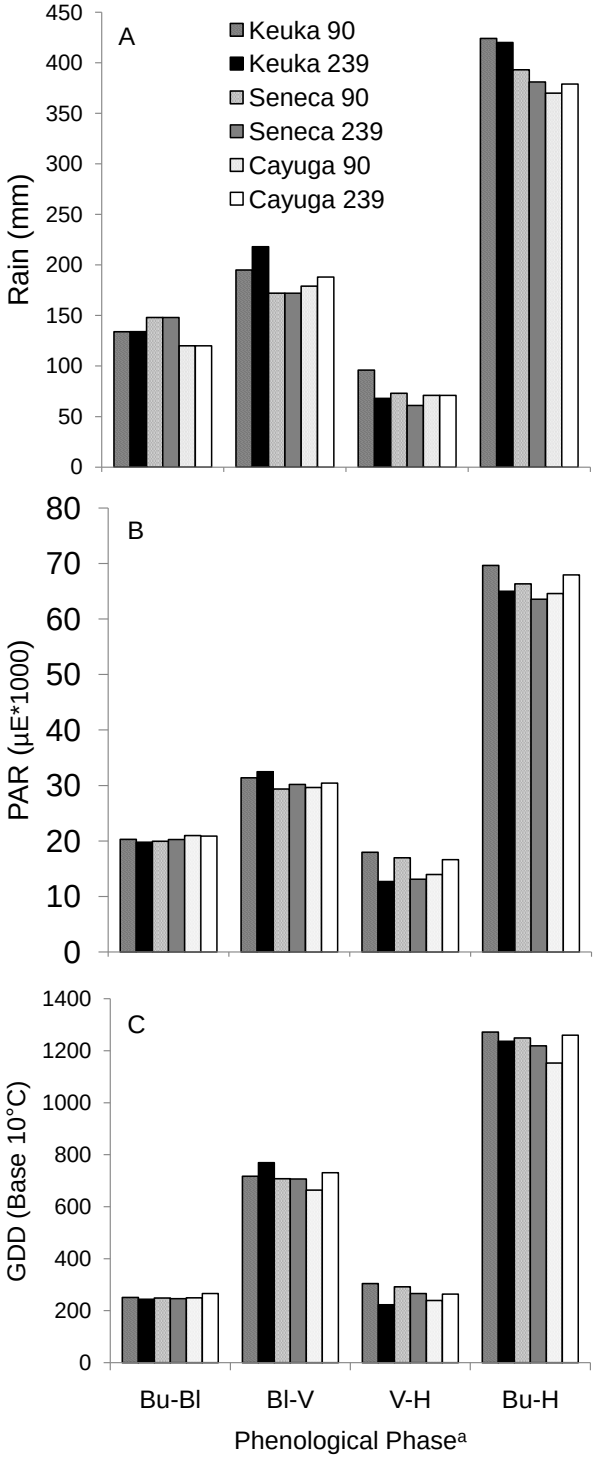

Figure 2.1 Climatic characteristics according to phenological phase. A) Total Rain Accumulation (mm), B) Sum of Average Daily Photosynthetically Active Radiation (µE*1000), C) Growing Degree Days (Base 10°C). [a]Phenological phases: Bu-Bl, Budbreak-Bloom; Bl-V, Bloom-Veraison; V-H, Veraison-Harvest; Bu-H, Budbreak-Harvest.

area ratio of the compound of interest to the internal standard, 2-octanol. Calibration curves were constructed using Microsoft Excel (Redmond, WA).

2.2.10 Statistical analyses. Statistical analyses were conducted using SAS JMP version 8.0 (Cary, NC) for analysis of variance (ANOVA) and student's t-test. Hierarchical cluster analyses were performed using Minitab version 16 (State College, PA). Standard deviations, standard errors (SE), and 95% confidence intervals were calculated using Microsoft Excel 2007 (Redmond, WA).

2.3 Results and discussion

2.3.1 Vintage and Riesling vineyard site characteristics. Climatic data varied by site as shown in Figure 2.1. Rain, PAR, and GDD accumulation were greatest during the longest phenological period from bloom to veraison. The 2009 vintage was relatively cool and cloudy; GDD and precipitation were below the long-term average for the region over the entire season. However, there was measurable precipitation on the majority of days in late June and early July, which greatly impacted bloom, fruit set, and grapevine growth in the middle of the growing season (Walter-Peterson 2009). The cooler temperatures likely resulted in wetter soils by decreasing the rate of soil drying. Therefore, 2009 was considered a wet year in the Finger Lakes region despite data suggesting otherwise.

Soil health analyses (Table 2.4) revealed three distinct textural classes among the vineyard sites: loam, silt loam, and sandy loam. ANOVA by lake for all soil factors resulted in significance ($p<0.05$) for only sand and silt, of which Seneca Lake was significantly different from Cayuga and Keuka Lakes (data not shown). Clay content was similar across sites. These results indicate that the soil characteristics of the vineyards were site specific. The major chemical difference in the vineyard soils was pH, which was associated with soil nutrient variations. Mg concentrations and

potentially mineralizable nitrogen were lower in more acidic soils at Keuka 90 and Seneca 239 vineyards. Conversely, soil Mn and Al concentrations were higher, likely due to greater solubility of these cations in the soil solution (Wolf 2007). Although 3309 rootstock is rated as sensitive to acidic soil conditions (Wolf 2007), soil pH variability in these Finger Lakes vineyards did not result in any vine nutrient deficiencies or toxicities (Table 2.5). A general trend of soil pH exists in the Finger Lakes such that soil pH decreases from north to south within the region, rather than east to west by lake, based on the associated parent material deposited by glaciers (Linhoff 2005). Soil liming, however, is standard practice in this region. Therefore, differences in soil pH most likely reflected variation in soil liming frequency. Nonetheless, grapevines grown in acidic, neutral, and alkaline soils have historically produced wines of high quality (Seguin 1986).

Table 2.4 Physical, biological, and chemical parameters of soil by vineyard site

Vineyard	Physical						
	Soil Type	Textural Class	Sand (%)	Clay (%)	Silt (%)	Aggregate Stability (%)	Available Water Capacity (%)
Keuka 90	Honeoye	loam	51.2	12.5	36.3	47.6	0.17
Keuka 239	Lansing	loam	49.7	8.2	42.1	36.3	0.14
Seneca 90	Lansing	silt loam	32.2	15.2	52.7	12.2	0.14
Seneca 239	Lansing	silt loam	32.4	11.4	56.3	20.6	0.18
Cayuga 239	Aurora	loam	47.9	10.9	41.2	12.6	0.15
Cayuga 90	Ovid	sandy loam	56.4	9.0	34.6	31.3	0.19
	Biological						
	Organic Matter (%)		Active Carbon (mg/kg)		Potentially Mineralizable N (µgN/g dry wt/week)		
Keuka 90	3.1		363.8		8.2		
Keuka 239	2.7		445.5		14.0		
Seneca 90	2.9		310.0		10.9		
Seneca 239	2.5		271.9		7.6		
Cayuga 239	2.5		369.2		12.4		
Cayuga 90	3.7		510.1		16.8		
	Chemical						
	CEC (cmol/kg)	pH	P (mg/kg)	K (mg/kg)	Mg (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Ca (mg/kg)	Al (mg/kg)
Keuka 90	13.1	4.9	6.5	141.3	71.3	36.5	13.8	1.5	540.0	88.8
Keuka 239	13.7	6.7	1.5	242.5	232.5	1.3	7.0	0.3	1347.5	10.0
Seneca 90	14.5	6.7	1.5	125.0	165.0	1.5	6.0	0.7	1802.5	12.5
Seneca 239	13.4	4.9	2.0	188.8	48.8	39.3	13.8	1.1	642.5	104.0
Cayuga 239	11.9	6.8	9.3	230.0	157.5	1.3	6.0	1.2	1242.5	9.8
Cayuga 90	15.9	6.1	1.5	168.8	318.8	1.5	6.5	1.4	1130.0	12.8

Table 2.5 Petiole nutrient concentrations by vineyard site compared to sufficiency ranges (Wolf 2007)

Vineyard	N[a]	K[a]	P[a]	Ca[a]	Mg[a]	Mn[b]	Fe[b]	Cu[b]	B[b]	Zn[b]
K90	0.860	1.55	0.138	1.63	0.355	465.5	26.3	9.75	32.0	66.3
K239	0.920	1.69	0.313	2.08	0.472	51.1	17.8	9.10	26.1	49.2
S90	0.865	2.33	0.139	1.93	0.414	86.7	70.9	10.10	32.5	46.2
S239	0.930	2.53	0.119	1.40	0.282	425.0	41.0	7.15	32.6	55.0
C239	0.875	1.62	0.149	1.81	0.486	102.2	24.1	11.95	28.7	42.9
C90	0.945	2.21	0.153	1.56	0.478	130.0	144.6	9.40	31.5	49.3
	Sufficiency Ranges									
Min	1.2	1.5	0.17	1.0	0.3	25	30	5	25	30
Max	2.2	2.5	0.30	3.0	0.5	1000	100	15	50	60

[a]Values are listed as %.
[b]Values are listed as mg/kg.

As previously stated, petiole analyses showed that most vine nutrient concentrations fell within sufficiency ranges (Table 2.5); therefore, any inherent differences in soil profiles were not manifested to considerable extent in the vines. Nitrogen and phosphorus petiole concentrations were slightly below the sufficiency ranges, but these low values were common among most vineyard sites, and may be attributed to excessive rainfall in the beginning of the season compounded by cool, cloudy weather.

2.3.2 Riesling must and wine composition. While there are many different indices used to evaluate grape maturity, including Brix, sugar to acid ratio, and malic to tartaric acid ratio (Bisson 2001), all Rieslings reached a consistent level of ripeness based on Brix level during the unseasonably cool 2009 vintage, and musts were within ±0.2 of the 21 Brix target for harvest (Table 2.6). This similarity illustrated the compatibility between the Riesling grape varietal and growing conditions in the Finger Lakes. Fruit maturity, in reference to harvest date (Table 2.1), did not depend on particular growing conditions by lake. In other words, no particular lake mesoclimate resulted in a specific maturity date, either earlier or later than the others. Higher level of Brix did not coincide with lower measurements of acidity, and the high acids may have been a manifestation of seasonal weather conditions. Timing of harvest has been

identified as an influential factor on wine quality, and increased hang time could have altered must and wine compositions (Gomez-Miguez et al. 2007). Seneca 239, Cayuga 90, Keuka 239 must compositions may have been impacted more by additional hang time since these sites were harvested earlier. In contrast, Seneca 90, Cayuga 239, and Keuka 90 harvests were later at the time of first frost when canopy photosynthetic capacity had diminished.

Table 2.6 One-way ANOVA by vineyard and two-way ANOVA by lake and clone for juice chemistry values (average of field replicates[a])

Vineyard	Brix	pH	TA[b] (g/L)	Tartaric Acid (g/L)	Malic Acid (g/L)	YAN[c] (mg/L)
One-way ANOVA						
K90	21.2a[d]	3.15a	12.86a	9.2a	4.5ab	277a
K239	20.8b	3.00b	13.69b	9.8ab	4.8a	157b
S90	20.8b	3.09c	13.01a	10.1bc	4.3ab	210c
S239	20.8b	3.10c	10.87c	9.8ab	3.1c	96d
C239	21.1a	3.00b	13.82b	10.6c	4.3ab	125e
C90	20.9b	3.25d	11.79d	9.2a	4.1b	236f
Significance[e]	0.0022	<0.0001	<0.0001	0.0214	0.0022	<0.0001
Two-way ANOVA						
Lake[e]	0.0156	0.0055	0.0001	0.1462	0.0020	<0.0001
Clone[e]	0.0924	<0.0001	0.0549	0.0170	0.0804	<0.0001
Lake*Clone[e]	0.0009	<0.0001	<0.0001	0.0225	0.0046	0.2738

[a]Each replicate was analyzed in duplicate.
[b]Titratable acidity, measured as tartaric acid equivalents.
[c]Yeast assimilable nitrogen
[d]Means followed by different letters in a column are significant at p<0.05 (Student's t).
[e]p-values, significant at p<0.05

One- and two-way ANOVA for juice chemistry values are listed in Table 2.6. There were significant interactions for all parameters except YAN. Must YAN levels in this study were site-specific, which was consistent with previous YAN surveys from the western United States (Butzke 1998) and New York State (Martinson and Gerling 2010). However, there was a trend for higher YAN content in clone 90 musts compared to clone 239 musts, which raises the question of whether the accumulation of nitrogen in berries is dependent on clone. Lake was also a main effect; Keuka Lake musts had the highest YAN while Seneca Lake musts had the lowest YAN. YAN has

been a topic of much debate, as yeast metabolism is the ultimate driver for conversion and production of aroma precursors into volatile compounds during fermentation. While it is preferential to control YAN levels through vineyard management practices, winemaking protocols to alter YAN status can have profound effects on wine quality (Bell and Henschke 2005). Thus, this factor has the potential to differentiate wines produced from unique vineyard sites. Table 2.7 lists the final basic wine chemistry data according to vineyard site at bottling.

Table 2.7 Wine chemistry by vineyard (mean ± SE of fermentation replicates)

Vineyard	pH	TA[a] (g/L)	RS[b] (g/L)	% Ethanol (v/v)
K90	3.11±0.01	10.2±0.07	6.3±0.7	13.0±0.1
K239	3.15±0.01	10.4±0.08	2.9±0.9	13.1±0.1
S90	3.16±0.02	9.3±0.09	7.3±0.1	11.8±0.0
S239	3.01±0.01	10.1±0.04	5.5±1.1	13.5±0.5
C90	3.07±0.01	10.1±0.04	2.3±0.0	13.4±0.1
C239	3.09±0.00	9.9±0.03	3.1±1.2	12.8±0.1

[a]Titratable acidity, [b]Residual sugar

2.3.3 Aroma chemistry of Riesling wines. Wine aroma profiles consisted of both grape- and fermentation-derived compounds (Table 2.8). The latter aroma constituents, including fatty acids, ethyl and acetate esters, and higher alcohols, were present in the highest concentrations, common among wines of all varieties. The most odor-active groups, assessed by comparison to sensory perception thresholds listed in Table 2.3, were acids and esters, with ethyl hexanoate present at the highest concentrations exceeding its sensory threshold. Ethyl hexanoate was also among the most odor-active compounds quantified in Australian Rieslings (Smyth 2005). One-way ANOVA for each compound by vineyard illustrated that 13 of the 26 compounds were different among vineyard sites (Table 2.8). The majority of these compounds belonged to the esters group, and in most cases, differences did not exceed a factor of 2. This trend was also true for the fatty acids. In general, despite the statistical significance by ANOVA, concentrations were similar across all wines.

Table 2.8 One-way ANOVA by vineyard and two-way ANOVA by lake and clone for aroma compound composition of Riesling wines (mean of fermentation replicates

Vineyard	Acids			Esters					
	Hexanoic Acid	Isovaleric Acid	Octanoic Acid	Diethyl Succinate	Ethyl Hexanoate	Ethyl Lactate	Hexyl Acetate	Isoamyl Acetate	β-Phenethyl Acetate
One-way ANOVA									
K90	9190[b]	953ab[c]	12021a	2103a	1852ab	4715ab	455a	2242a	-[d]
K239	7579	690c	8318b	1430bc	1470c	3046c	281b	880b	-
S90	9076	1103a	10326c	1365b	1704ac	5026a	304b	1140bc	-
S239	8613	635c	10578ac	1856d	1946b	6560d	271b	1443c	-
C239	8992	781bc	10321c	1765de	1988b	3835ce	415a	2219a	-
C90	7930	844bc	9512bc	1608ce	1605c	3986be	441a	1872a	-
Significance[e]	0.158	0.014	0.011	0.002	0.010	0.0005	0.002	0.001	- -[f]
Two-way ANOVA									
Lake[e]	0.550	0.654	0.487	0.146	0.111	0.0002	0.002	0.002	- -
Clone[e]	0.373	0.002	0.043	0.887	0.200	0.633	0.005	0.054	- -
Lake*Clone[e]	0.055	0.049	0.003	0.0003	0.003	0.001	0.024	0.001	- -

Vineyard	Alcohols							
	1-Butanol	1-Hexanol	2-Phenylethanol	Benzyl Alcohol	*cis*-3-Hexenol	Isoamyl Alcohol	Isobutanol	Methionol
One-way ANOVA								
K90	2138a	2239	10173ab	30	63	107759	15171	472b
K239	2010b	2457	10501a	41	93	76178	11686	526b
S90	2131a	2285	8959ab	38	94	93445	13833	885a
S239	2073c	2320	6280c	37	81	74932	11423	979a
C239	2097ac	2502	9576ab	28	91	91482	10234	654b
C90	2109ac	2527	8355b	23	82	94328	11587	494b
Significance[e]	0.006	0.628	0.018	0.168	0.626	0.081	0.080	0.003
Two-way ANOVA								
Lake[e]	0.161	0.360	0.010	0.077	0.756	0.411	0.098	0.001
Clone[e]	0.001	0.540	0.458	0.204	0.463	0.017	0.023	0.073
Lake*Clone[e]	0.020	0.692	0.035	0.526	0.358	0.177	0.579	0.674

[a]Fermentation replicates were analyzed in duplicate.
[b]All values listed in µg/L.
[c]Means followed by different letters in a column are significant at $p<0.05$ (Student's t).
[d]Below the limit of quantification.
[e]p-values, significance set at $p<0.05$.
[f]Insufficient data points to perform ANOVA.

Table 2.8 Continued

Vineyard	Volatile phenols		Monoterpenes					Norisoprenoids	
	4-Vinyl guaiacol	4-Vinyl phenol	*cis*-Rose Oxide	Citronellol	Geraniol	Linalool	Nerol	TDN	β-Damascenone
One-way ANOVA									
K90	126[b]	633	-[d]	3.4	14.6a[c]	21.1ab	-	0.3a	2.3
K239	122	474	-	3.2	7.9b	17.4c	-	-	1.2
S90	133	685	-	2.9	8.2b	24.0a	-	0.8b	1.8
S239	117	416	-	4.5	14.6a	44.2d	-	1.0b	1.3
C239	131	404	-	3.3	9.9b	18.3bc	-	0.3a	1.5
C90	109	497	-	3.3	9.2b	15.8c	-	-	1.8
Significance[e]	0.792	0.151	- -[f]	0.756	0.028	<0.0001	- -	0.015	0.111
Two-way ANOVA									
Lake[e]	0.922	0.345	- -	0.820	0.358	<0.0001	- -	- -	0.756
Clone[e]	0.953	0.028	- -	0.498	0.926	0.0001	- -	- -	0.017
Lake*Clone[e]	0.400	0.523	- -	0.479	0.007	<0.0001	- -	- -	0.254

[a]Fermentation replicates were analyzed in duplicate.
[b]All values listed in µg/L.
[c]Means followed by different letters in a column are significant at $p<0.05$ (Student's t).
[d]Below the limit of quantification.
[e]p-values, significance set at $p<0.05$.
[f]Insufficient data points to perform ANOVA.

Interestingly, Keuka 90 Rieslings had the highest concentrations for over half of the acids, esters, and alcohols, which could be a direct result of higher YAN content (Table 2.6). Higher YAN concentrations typically result in more fermentation-derived compounds in wine (Swiegers et al. 2005). In addition, the form of YAN present in a fermentation has been shown to impact wine aroma composition. Hernandez-Orte et al. (2002) found that amino acid composition affected production of specific volatiles in synthetic wines. It is also possible that the YAN supplementation protocol standardized production of certain aroma compounds during alcoholic fermentation. Since clone 239 Rieslings were lower in YAN, the aroma compound composition of these wines may have been noticeably different without supplementation with diammonium phosphate. On the other hand, lack of supplementation may also have led to stuck fermentations. Two-way ANOVA (Table 2.8) showed either no significant differences and/or significant interactions for most aroma compounds. On average, Seneca Lake wines had the highest concentrations of methionol while Keuka Lake wines had the lowest. Yeast metabolize the amino acid methionine into methionol which contributes negative reduction aromas to wines (Ribereau-Gayon et al. 2006), but concentrations in all Rieslings were below the reported sensory threshold. The four compounds with main clone effects were isoamyl alcohol, isobutanol, 4-vinylphenol, and β-damescenone. Clone 90 consistently had higher concentrations than clone 239, and of those volatiles, only β-damescenone would contribute positively to Riesling varietal aroma. Rapp (1998) reported that 4-vinylphenol, in particular, may have negative implications for wine aroma when combined with 4-vinylguaiacol. At concentrations exceeding 800 µg/L, which were correlated with sun-exposed fruit, Kerner wines expressed a medicinal or Band-aid aroma. In the research wines, no differences existed for 4-vinylguaiacol, and no clear viticultural patterns could be related to the significant differences in 4-vinylphenol concentrations. The sensory

threshold was met in some of the clone 90 wines, and clonal variation was the most logical explanation.

Linalool was the only monoterpene present at concentrations above sensory threshold. However, it is probable that the monoterpenes have an additive effect, thus contributing to the overall floral aromas in Riesling. Seneca 239 wines were notable for relatively high concentrations of linalool compared to the other wines. Unlike Rieslings from other regions (Skinkis et al. 2008, Smyth 2005), nerol and *cis*-rose oxide were not detected in the Finger Lakes wines although the former, along with other monoterpenes, may appear after bottle age due to acid-catalyzed rearrangement from linalool (Ebeler 2001). Geraniol concentrations were significantly higher in Seneca 239 and Keuka 90 wines, and these vineyards were lowest in vine water status among the sites (Table 2.9). Geraniol concentrations did not exceed the sensory threshold, consistent with results from a survey of Finger Lakes Rieslings (Gates and Sacks, unpublished data). Although linalool and citronellol did not individually follow the same trend as geraniol related to vine water status, Seneca 239 and Keuka 90 had the highest concentrations of monoterpenes collectively. Willwerth et al. (2010) found monoterpene concentrations positively correlated with vine water status, but that berry size may have been a confounding variable. They suggested an optimal level of water status may exist in a region of mild water stress, while no water stress or high water stress both result in decreased monoterpenes. Collective assessment of $\delta^{13}C$ values for leaves and berries at veraison and harvest showed a small range, and revealed no water deficits for any of the six sites in this study when compared to the varying degrees of water status from severe (> -21.5‰) to no water deficit (< -26‰) (van Leeuwen et al. 2008). Moreover, these results may reflect the fact that 2009 was a relatively cool and cloudy growing season in the Finger Lakes, and climate and vintage have been shown to significantly impact vine water status in grapevines (van Leeuwen et al. 2004,

Gaudillere et al. 2002, Willwerth et al. 2010). Even though none of the vines were under water stress, the sites with lower water status could have been closer to optimal levels for increased berry monoterpene synthesis.

Table 2.9 $\delta^{13}C$ (‰) of leaf and berry samples at veraison and harvest by vineyard site

Vineyard	Leaves		Berries	
	Veraison	Harvest	Veraison	Harvest
K90	-27.05	-27.56	-25.88	-26.15
K239	-28.25	-28.46	-28.08	-28.57
S90	-27.14	-28.04	-27.14	-27.72
S239	-26.55	-27.10	-26.07	-26.25
C90	-28.21	-28.67	-28.11	-28.22
C239	-28.19	-28.61	-28.39	-29.02

Monoterpenes have also been associated with differences in canopy light environment and crop level (Reynolds and Wardle 1989). Table 2.10 and 2.11 list measurements of canopy architecture and yield components, respectively, which varied by vineyard site despite standardized shoot and cluster thinning. Significant differences were found by lake and clone for all canopy architecture metrics except CEFA by clone, which was approaching significance. Interactions were also significant excluding CEL; therefore, lake and clone were both main effects for CEL. While EPQA suggested differences in canopy density and light environment among sites, these differences were smaller than panels compared within a small block of a well-managed Riesling vineyard (Meyers 2010). Monoterpenes have been shown to decrease with more shading in aromatic white varietals (Reynolds et al. 1994, Reynolds and Wardle 1989, Skinkis et al. 2010); however, Meyers (2010) found few differences in flavor and aroma chemistry in Riesling wines produced from vines with a comparable range of CEFA values as this study. Thus, statistical significance did not

translate into practical significance for differences in canopy density and light environment.

Table 2.10 One-way ANOVA by vineyard and two-way ANOVA lake and clone for canopy density and light environment metrics (mean ± SE of ten replicate panels) at veraison

Vineyard	OLN[a]	CEL[b]	CEFA[c]	LEFA[d]
One-way ANOVA				
K90	2.99±0.09a[e]	0.64±0.04a	26.7±1.9ab	41.1±0.8a
K239	2.05±0.06b	0.45±0.04b	39.0±1.9c	53.6±1.4b
S90	2.40±0.06c	0.45±0.02b	47.9±1.5d	57.3±1.2c
S239	2.33±0.07bc	0.43±0.03b	37.6±1.9c	49.0±0.9d
C239	2.90±0.14a	0.70±0.07ac	28.3±3.4a	43.9±1.9a
C90	3.36±0.14d	0.82±0.05c	21.2±1.3b	37.0±1.0e
Significance [f]	<0.0001	<0.0001	<0.0001	<0.0001
Two-way ANOVA				
Lake[f]	<0.0001	<0.0001	<0.0001	<0.0001
Clone[f]	<0.0001	0.0043	0.0809	0.0006
Lake*Clone[f]	0.0003	0.1762	<0.0001	<0.0001

[a,b,c,d]Occlusion layer number, cluster exposure layer, cluster exposure flux availability reported as %, leaf exposure flux availability reported as %, respectively.
[e]Values followed by different letters in a column are significant at p<0.05 (Student's t).
[f]p-values, significant at p<0.05.

Table 2.11 One-way ANOVA by vineyard and two-way ANOVA by lake and clone for harvest yield components (mean ± SE of ten replicate panels)

Vineyard	Cluster wt (g)	Berry wt (g)	Berries per cluster	Clusters per m	Fruit wt per m (kg)	Pruning wt per m (kg)	Crop load
One-way ANOVA							
K90	95.9±7.8a[a]	1.20±0.05a	79±4.6a	32±1.5a	3.00±0.20a	0.29±0.03a	11.3±1.2a
K239	74.3±3.2b	1.06±0.03ab	70±1.5a	28±1.0ab	2.09±0.14b	0.39±0.02bc	5.4±0.2bc
S90	105.8±2.8a	1.06±0.03ab	101±3.5b	29±0.7ab	3.10±0.10a	0.35±0.01ab	9.0±0.4d
S239	80.6±4.3b	1.46±0.11c	58±4.8c	26±0.8b	2.07±0.06b	0.44±0.01c	4.7±0.2b
C239	72.0±2.9bc	0.98±0.04b	74±2.5a	32±2.7a	2.26±0.21bc	0.28±0.02a	8.2±0.5de
C90	60.5±5.0c	1.05±0.04ab	57±3.7c	44±2.2c	2.70±0.27ac	0.41±0.05bc	6.8±0.4ce
Significance[b]	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0002	<0.0001
Two-way ANOVA							
Lake[b]	<0.0001	0.0003	0.0014	<0.0001	0.8501	0.0775	0.0423
Clone[b]	0.0030	0.1881	0.0002	<0.0001	<0.0001	0.3347	<0.0001
Lake*Clone[b]	0.0003	<0.0001	<0.0001	0.0092	0.2277	<0.0001	<0.0001

[a]Values followed by different letters in a column are significant at p<0.05 (Student's t).
[b]p-values, significant at p<0.05.

Similar to canopy architecture results, yield components were significantly different ($p<0.001$) by vineyard site despite shoot and cluster thinning. Clusters per meter were comparable with the exception of C90 which was higher than any other vineyard site and may be attributed to non-count shoots. Two-way ANOVA results were significant for most of the variables by lake and clone; however, there were interactions for all but fruit weight per meter. Clone 90 had significantly more fruit weight per meter compared to clone 239, though there was no specific variable among cluster weight, berry weight, or berries per cluster that contributed to the difference. The range of fruit weight per meter translated to roughly 3 to 5 tons per acre among the sites. Crop load values ranged from 4.7 to 11.3 among the sites, and all except Keuka 90 and Seneca 239 were within the recommended range (5 to 10) where crop load does not negatively impact wine quality (Bravdo et al. 1985, Dry et al. 2005). However, cropping studies in Riesling suggested no effects on wine quality for crop loads ranging from 6.4 to 19.7 (Reynolds et al. 1994), indicating that quality fruit can be produced from a wide range of crop loads in Riesling. In summary, the yield components among sites most likely had no effect on wine quality due to the relatively small differences around the recommended ranges for premium wine grape production.

TDN concentrations were at or below 1 µg/L in all wines and below the quantification limit (0.3 µg/L) in Keuka 239 and Cayuga 90 wines. These concentrations of free TDN were less than those previously quantified in 2008 Finger Lakes Rieslings of similar age at the time of analysis (Kwasniewski et al. 2010). One possible explanation for the difference is the vintage. The cool and cloudy 2009 season may have resulted in lower TDN concentration in berries compared to the warmer, sunnier 2008 vintage, as both increased temperature and sun-exposed fruit have been positively correlated with TDN concentrations (Marais et al. 1992,

Linsenmeier and Lohnertz 2007). While there were significant differences among the wines in this study, with Seneca Lake wines having more TDN than the others, the overall range was small, and correlations to light environment metrics were not evident. A survey of 32 Finger Lakes Rieslings with 1 to 2 years of bottle age, mainly from 2005 and 2006 vintages, also showed higher concentrations of TDN (median 6 µg/L) (Gates and Sacks, unpublished data). Since TDN concentrations increase over time via acid hydrolysis of TDN precursors (Rapp 1998), bottle age may account for a large part of the concentration differences seen among our experimental Rieslings and the commercial wines. Although commercial Finger Lakes Rieslings are typically bottled and released within the year following vintage and consumed relatively early, quantification of TDN precursors would provide a clearer understanding of whether TDN has the potential to differentiate research wines by vineyard site after more bottle aging.

2.3.4 Sensory analysis of Riesling wines. Eleven aroma attributes were generated by descriptive analysis to characterize the Riesling wines, including pineapple, melon, raspberry, dried fruit, citrus, linalool/floral, clove, caramelized, earthy, stemmy, and petrol. This list of terms was consistent with the predominantly fruity and floral aromas used to describe Riesling in other regions (Cozzolino et al. 2006, Reynolds et al. 1994, Douglas et al. 2001, Fischer et al. 1999, Fischer et al. 2009, Willwerth et al. 2010, Smyth 2005). Figure 2.2 illustrates the perceived attribute intensities in the wines by vineyard. The wine aroma profiles were similar across vineyard sites, which their similar aroma chemistry suggests. Citrus had the highest intensity ratings for all wines, and pineapple was consistently rated second. Linalool/floral, melon, and stemmy notes were also among the most intensely perceived. German Rieslings fermented with the same commercial yeast strain resulted in several overlapping terms/ingredients: floral, cantaloupe/melon, pineapple,

and citrus. Green notes were also identified, but their descriptors were green bean and green grass (Fischer et al. 2009). Grassy was originally included in the list of attributes for Finger Lakes Rieslings, but the sensory panel eliminated grassy and retained stemmy instead.

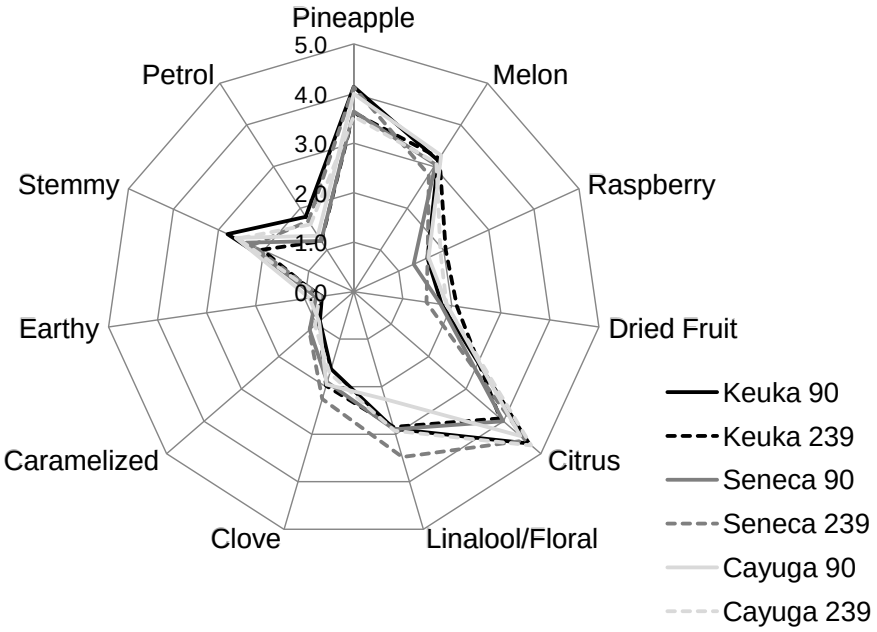

Figure 2.2 Average intensity ratings on a 12-cm scale of attributes for combined replicate fermentations according to vineyard analyzed by descriptive analysis.

Three-way ANOVA performed on all wines by aroma attribute resulted in no significant differences (Table 2.12). Linalool/floral, raspberry, and stemmy were the top three aroma attributes closest to significance with p-values of 0.099, 0.174, and 0.277, respectively. Sensory data for linalool/floral correlated to the aroma chemistry; Seneca 239 wines had the highest concentrations of linalool and were rated as having the highest linalool/floral intensities. Conversely, Cayuga 90 wines had the lowest concentrations of linalool, and panelists perceived linalool/floral aromas the least in these wines. While no other direct correlations were observed between sensory aroma intensities and chemical data, many of the sensory descriptors were associated with the quantified aromatics. The fatty acid esters and β-damascenone may have contributed

to fruity aromas, and the latter may also enhance the caramelized attribute. 1-Hexanol and *cis*-3-hexenol, grape-derived compounds having green odorant descriptors (Dunlevy et al. 2009), would be likely candidates for the stemmy aromas, but they were below the sensory thresholds. Kalua and Boss (2010) recently monitored the metabolism of these C_6 alcohols, which were shown to be present in Riesling berries. Lastly, the characteristic Riesling petrol aroma is associated with TDN. Although TDN was below its published perception threshold (20 µg/L) (Simpson et al. 1978); recent work by Acree and colleagues (unpublished data) using a TDN standard suggested that the perception threshold for TDN in wine is somewhere between two- to six-fold lower than the level previously reported. Additionally, results indicated that TDN may change the sensory perception of wines when present at concentrations as low as 2 µg/L, even if its corresponding petrol character goes unrecognized. Although the concentration of TDN in all of the wines was very low, Seneca 239 and Seneca 90 were just below this latter threshold. Because detection thresholds are established by at least fifty percent of the population perceiving a difference, it is possible that the levels reported in these Rieslings were recognized as petrol by some of the panelists.

Table 2.12 p-values from three-way ANOVA for experimental wines by aroma attribute

Attribute	Judge		Wine		Rep		Wine X Judge		Judge X Rep		Wine X Rep	
Pineapple	<.0001	***	0.521	ns	0.010	**	0.704	ns	0.095	ns	0.077	ns
Melon	<.0001	***	0.930	ns	0.043	*	0.407	ns	0.004	**	0.977	ns
Raspberry	<.0001	***	0.174	ns	0.089	ns	0.372	ns	0.080	ns	0.943	ns
Dried Fruit	<.0001	***	0.403	ns	0.167	ns	0.117	ns	0.004	**	0.185	ns
Citrus	<.0001	***	0.485	ns	0.478	ns	0.576	ns	0.678	ns	0.565	ns
Lin/Floral	<.0001	***	0.099	ns	0.004	**	0.803	ns	0.005	**	0.915	ns
Clove	<.0001	***	0.897	ns	0.966	ns	0.248	ns	<0.0001	***	0.743	ns
Caramelized	<.0001	***	0.630	ns	0.105	ns	0.569	ns	0.590	ns	0.927	ns
Earthy	<.0001	***	0.446	ns	0.195	ns	0.980	ns	0.061	ns	0.276	ns
Stemmy	<.0001	***	0.277	ns	0.034	*	0.422	ns	0.120	ns	0.532	ns
Petrol	<.0001	***	0.756	ns	0.000	***	0.950	ns	0.008	**	0.309	ns

*,**, ***, and ns indicates significance at $p < 0.05$, 0.01, 0.0001, and not significant, respectively.

It is possible that the similarity of the wines resulted in more inconsistent ratings by panelists attempting to find differences during sensory analysis. Pineapple, melon, linalool/floral, stemmy, and petrol attributes were all significant by sensory replicate (Rep) indicating some inconsistent ratings between the first and the second sensory replicate. Mean scores of the second sensory replicate were lower for all attributes except clove and caramelized, which could signify adaptation by the panel over time. Significant interaction between judge and replicate (Judge X Rep) for melon, dried fruit, linalool/floral, clove, and petrol indicated some judge irreproducibility. Results showed that judges were the greatest source of variance, with all attributes significant by judge, indicating that panelists used different parts of the line scale, which is common in descriptive analysis (Stone et al. 1974). Though panelists were trained with the same intensity scale, they likely perceived intensities by aroma differently based on individual sensitivities. Thus, the intensity training was more useful for individual consistency and reproducibility. Two-way ANOVA results by lake and clone were not significant for any attributes (data not shown).

2.3.5 Phenolic acids in Riesling wines. Figure 2.3 depicts a representative HPLC chromatogram of Finger Lakes Riesling wine at 320 nm. The HCAs and their respective tartrate esters were all present at quantifiable levels. Catechin eluted at 18.0 minutes, directly after caftaric acid, which is not visible at the wavelength shown. Gallic acid (10.8 min) and epicatechin (21.6 min) were below the limits of quantification. However, other compounds were eluting close to both compounds which may have interfered with quantification. Several peaks remained unidentified, with the most notable unknown peak at 14.1 minutes. This peak consistently had the second highest peak area among all Rieslings. The absorption spectrum with maximum absorptions at 254 and 330 nm would suggest that this compound is a HCA derivative. Compounds eluting after 40 minutes were most likely conjugates of

quercetin based on their maximal absorbances around 370 nm. Further analysis by LC/MS would be necessary for confirmation.

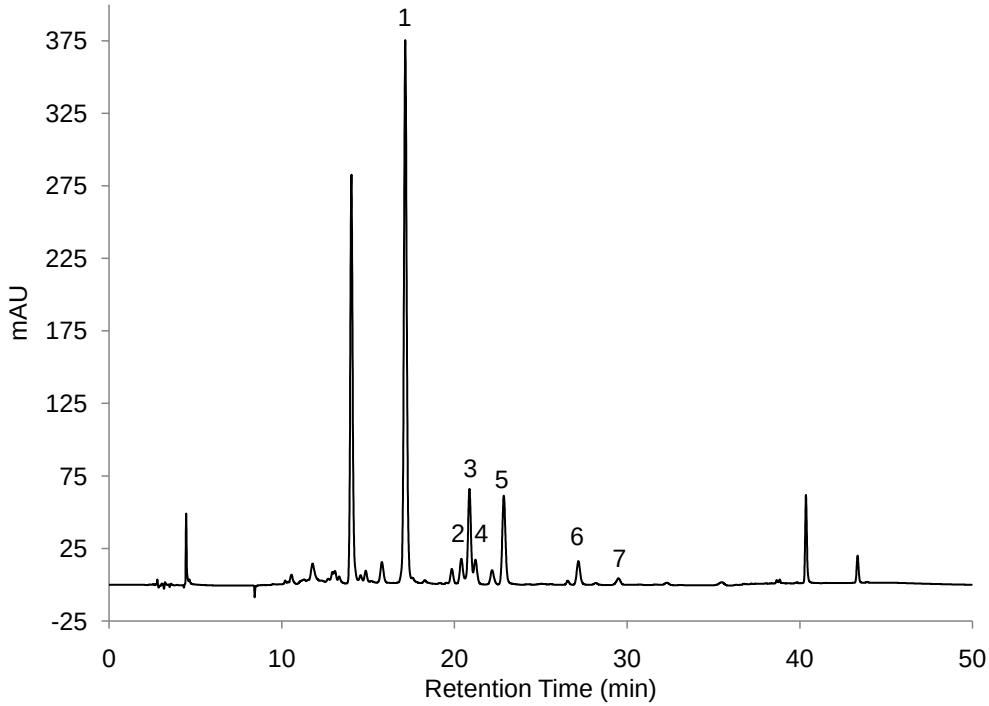

Figure 2.3 HPLC chromatogram of Riesling wine at 320 nm. Hydroxycinnamic acids and their tartrate esters include: 1) caftaric acid, 2) *cis*-coutaric acid, 3) caffeic acid, 4) *trans*-coutaric acid, 5) coumaric acid, 6) fertaric acid, and 7) ferulic acid.

The concentrations of phenolic acids in Rieslings are listed in Table 2.13. The ANOVA by vineyard site showed significant differences for each compound. Ferulic and caftaric acids were present in the lowest and highest concentrations in the Rieslings, respectively. Comparatively higher levels of caftaric acid have previously been shown to distinguish Riesling from other white varieties (Ong and Nagel 1978). Catechin had the smallest relative range among vineyard sites with the highest level at 1.4 times the lowest level; *trans*-coutaric acid varied the most with C239 containing 11.2 times as much compound as S90. Caffeic acid concentrations were most comparable to those reported by Goldberg et al. (2000) for eighteen commercial

Finger Lakes Rieslings. Of the other compounds quantified in both analyses, catechin (~1 mg/L) was lower and p-coumaric acid (~2 mg/L) was higher in their study, respectively. Unfortunately, standard deviations were not provided to capture the variation of concentrations among wines. Further, epicatechin and gallic acid were quantified by GC-MS, while the HPLC analysis used in the current study was not sufficiently selective for quantification. HCA tartrate ester concentrations have not been previously reported for Finger Lakes Riesling, but results were comparable to levels previously reported within and among other regions such as Ontario (Kilmartin et al. 2007), Washington (Nagel et al. 1979), Germany (Pour Nikfardjam et al. 2007), and Australia (Somers et al. 1987). Fertaric acid concentrations exceeded coutaric acid concentrations in all experimental wines, a trend which has been identified in some (Kilmartin et al. 2007, Nagel et al. 1979, Soleas et al. 1997) but not all Riesling phenolic profile studies.

Table 2.13 One-way ANOVA by vineyard and two-way ANOVA by lake and clone for phenolic acid concentrations (mean ± standard deviation) of wine fermentation replicates[a]

Vineyard	Catechin[b]	Caffeic Acid	Caftaric Acid	Coumaric Acid	*cis*-Coutaric Acid	*trans*-Coutaric Acid	Ferulic Acid	Fertaric Acid
One-way ANOVA								
K90	3.4 ± 0.1	4.0 ± 0.04a[c]	21 ± 0.6a	0.98 ± 0.01a	1.0 ± 0.02a	1.0 ± 0.04a	0.31 ± 0.001a	4.1 ± 0.003a
K239	3.7 ± 0.5	2.6 ± 0.4b	47 ± 0.3b	0.61 ± 0.08bc	1.2 ± 0.04b	3.2 ± 0.3b	0.23 ± 0.01bc	4.3 ± 0.05b
S90	3.1 ± 0.02	5.2 ± 0.1c	19 ± 0.2ac	0.86 ± 0.002d	0.8 ± 0.03c	0.6 ± 0.05c	0.22 ± 0.01c	3.2 ± 0.02c
S239	3.5 ± 0.1	2.8 ± 0.3bd	39 ± 2.7d	0.56 ± 0.04c	1.1 ± 0.01d	2.3 ± 0.1d	0.14 ± 0.002d	4.0 ± 0.06d
C239	3.6 ± 0.2	1.0 ± 0.1e	62 ± 0.3e	0.22 ± 0.02e	1.3 ± 0.04b	5.5 ± 0.1e	0.21 ± 0.01c	4.7 ± 0.07e
C90	3.1 ± 0.3	3.4 ± 0.2d	17 ± 1.0c	0.70 ± 0.07b	0.8 ± 0.04c	0.7 ± 0.04ac	0.28 ± 0.05ab	3.3 ± 0.02c
Significance[d]	0.1679	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0041	<0.0001
Two-way ANOVA								
Lake[d]	0.3131	<0.0001	<0.0001	0.0002	0.0025	<0.0001	0.0045	<0.0001
Clone[d]	0.028	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0014	<0.0001
Lake*Clone[d]	0.8094	0.0349	<0.0001	0.1007	0.0023	<0.0001	0.9473	<0.0001

[a]Fermentation replicates were analyzed in duplicate by HPLC, and results were averaged.
[b]All values are listed in mg/L.
[c]Means followed by different letters in a column are significant at $p<0.05$ (Student's t).
[c]p-values, significance set at $p<0.05$.

Two-way ANOVA (Table 2.13) confirmed that clone was the strongest variable contributing to phenolic acid composition. Even though all phenolic acids were significant ($p<0.05$) by clone, and all except catechin were significant ($p<0.05$) by lake, the p-values for clone were lower for most compounds. Significant interactions ($p<0.05$) between lake and clone existed for caffeic, caftaric, cis-coutaric, trans-coutaric, and fertaric acids, suggesting that the clones behaved differently depending on the lake of origin. Figure 2.4 graphically represents the trend of phenolic acid profiles by clone; all phenolic acid compounds were statistically significant to varying degrees. Wines made from Riesling clone 90 had higher concentrations of free HCAs compared to Riesling clone 239, whereas the opposite was true for HCA tartrate esters. The clonal variation in phenolics may have both positive and negative implications for Riesling wines. Higher concentrations of caffeic and gallic acids have been shown to inhibit disappearance of aromatic esters and terpenes in wines (Lambropoulos and Roussis 2007), so clone 90 may provide more protection against loss of fruity and floral aromas than clone 239, due to the higher concentration of free HCAs. However, the pH of wine favors the conversion of HCA tartrate esters to free HCAs by acid hydrolysis (Waterhouse 2002); because clone 239 wines were higher in total HCAs (free plus tartrate esters), clone 239 may prevent aroma losses over time. More investigation is necessary to test these hypotheses. The detrimental effect of higher phenolic concentrations in wine is oxidative browning potential (Waterhouse 2002) which may have negative repercussions on the acceptability of Riesling wines. While HCAs are reported to have bitter and astringent flavor profiles, these characteristics are irrelevant based on the concentrations present in the Rieslings (Verette et al. 1988).

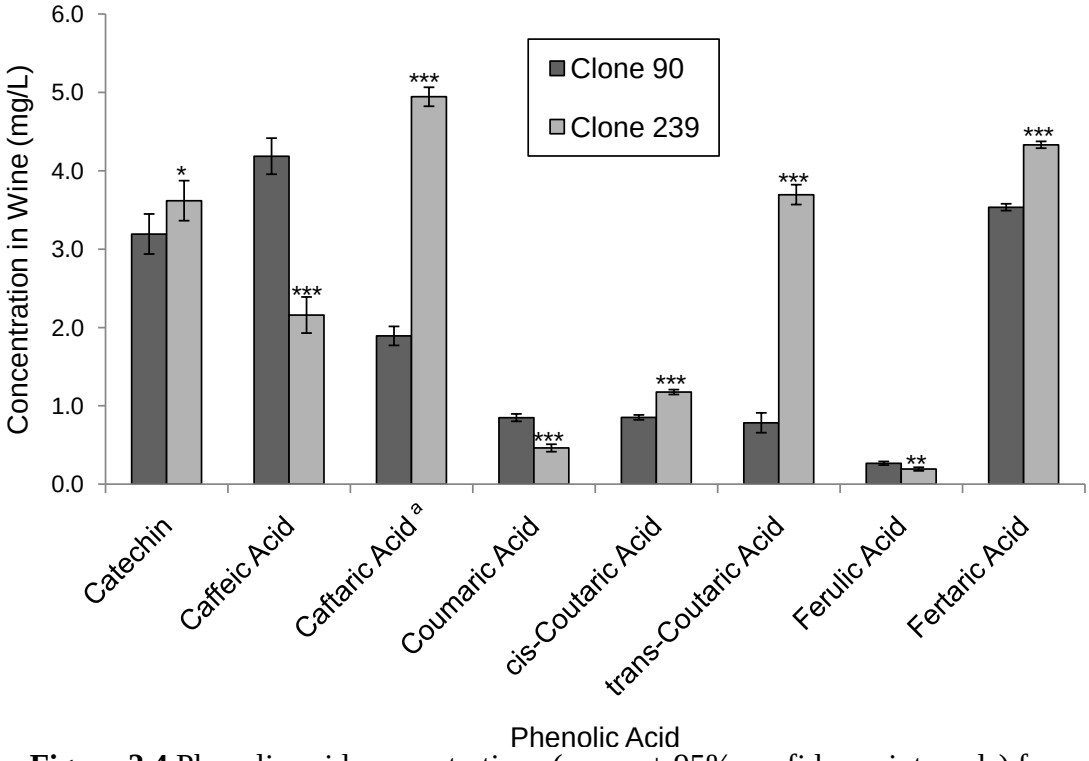

Figure 2.4 Phenolic acid concentrations (mean ± 95% confidence intervals) for fermentations pooled by clone. *, **, *** indicate statistical significance by compound at $p<0.05$, 0.01, and 0.001, respectively. [a]Caftaric acid concentration was scaled down 10-fold to fit the graph.

Final concentrations of phenolic acids were likely influenced by the winemaking protocol. Commercial pectinases have been shown to convert HCA tartrate esters to free HCAs through cinnamoyl esterase activity (Dugelay et al. 1993, Lao et al. 1997), and Lallzyme C was used for juice clarification prior to yeast inoculation in this study. Thus, the settling treatment may have stimulated the hydrolysis of HCA tartrate esters. The addition of pectinase to Riesling musts in the Finger Lakes is neither standard nor atypical, but may be a point of differentiation leading to a range of phenolic profiles among commercial Rieslings. Additionally, some *S. cerevisiae* yeast strains have enzyme activity to decarboxylate free HCAs into volatile phenol compounds (Chatonnet et al. 1993), specifically transforming coumaric and ferulic acid to 4-vinylphenol and 4-vinylguaiacol, respectively. As discussed

earlier, the concentrations of 4-vinylphenol differed by clone. One possible explanation is based on higher concentrations of coumaric acid substrate in clone 90 Rieslings, but without phenolic acid grape or must data, speculation is limited. The distribution of coumaric acid, coutaric acid, and 4-vinylphenol concentrations among the distinct clones did not account for the differences. The same held true for ferulic acid and its derivatives. This simplified approach has ignored the fact that not all HCA derivatives were quantified. Moreover, it is evident that other factors (i.e. viticultural) were involved in determining the final phenolic profiles. Regardless, the clonal material had a stronger influence on all phenolic structures, which may have an impact on winemaking decisions and outcomes.

2.3.6 Cluster analyses of viticultural, sensory, and compositional data.

Figure 2.5 graphically depicts the similiarity of the vineyards and fermentations among sites based on the different data sets collected in this study. Cluster analysis on the combined viticultural data did not result in primary or secondary linkages by lake, further illustrating the fact that lake association does not necessarily equate to similar growing conditions and viticultural characteristics. Of the three lakes, Cayuga Lake vineyards were most similar to one another. This result is interesting because of the training system and vine age differences between Cayuga sites. However, none of the six sites seemed to be unique to the extent at which differences would be anticipated in the wines based on evaluation of the individual components in previous sections. Thus, the sensory analysis of the wines pointed toward similarities rather than differences. All aroma compounds by wine revealed the similarity, thus reproducibility, of the fermentation replicates with the exception of the Cayuga Lake wines. The latter fermentation replicates did not link together first in the dendrogram, which may reflect inconsistencies of the replicate fermentations. On the other hand,

the aroma chemistry data was similar for all wines, so these apparent differences may be capturing statistically insignificant variations in volatile composition.

The dendrogram illustrates that no clear relationship existed by lake or clone for the pooled aroma chemistry data, since lakes and clones are interspersed along the x-axis. The limitation to approaching the data from this standpoint is that sensory thresholds were not taken into account. Thus, some of the compounds that were quantified in the wines may have little impact on the Riesling aromas, but they were incorporated into this cumulative comparison. Lastly, phenolic acid concentrations were consistent between duplicate fermentations using fruit from the same vineyard; primary linkages grouped all vineyards together to form six clusters. The final two clusters demonstrated that phenolic acid profiles were most similar by clone. However, the clone 90 fermentations were collectively more similar compared to the clone 239 fermentations since clusters were formed at a higher similarity value. Two lakes were not apparently more similar than the third; Seneca and Keuka Lakes clustered together first for clone 239 while Cayuga and Seneca Lakes clustered together first for clone 90.

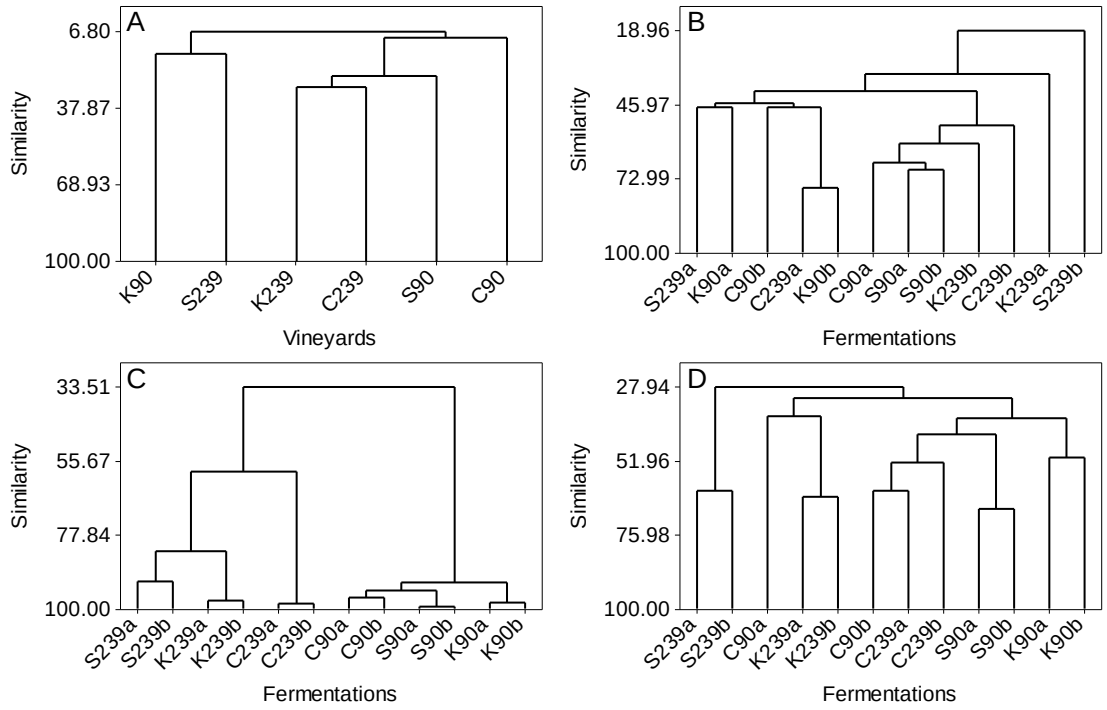

Figure 2.5 Dendrograms from hierarchical cluster analysis. A) viticultural, B) aroma chemistry, C) phenolics, and D) sensory data.

2.4 Conclusion

While statistically significant differences related to vine balance, canopy density, and water status were identified among the sites, the findings did not appear to have practical significance for grape and wine quality based on reference ranges of viticultural characteristics within and outside the Finger Lakes region. In support of these claims, viticultural differences were not large enough to substantially change Riesling wine composition or elicit distinct sensory profiles as perceived by a trained panel of white wine consumers. In summary, no clear patterns were established for Finger Lakes Riesling vineyards by lake or clone. Therefore, winemaking and vineyard management factors may play the biggest role in differentiating Rieslings within the region. Yeast assimilable nitrogen composition, in particular, has the potential to be a key player in Rieslings based on the wide range of inherent YAN

content observed in this study. The sensory assessment of the Rieslings shortly after bottling points toward the importance of fermentation-derived aroma compounds and little differentiation among young Riesling wines. Overall, the concentrations of aroma compounds were similar to those reported in Rieslings from other regions, and all of the aroma attributes generated by descriptive analysis were typical for Riesling as a varietal. No unique descriptor terms were developed for Finger Lakes Riesling aromas, but the sensory and aroma chemistry data for Finger Lakes Riesling is among the first to be reported for the region and adds to the limited data contributing to a definition of Finger Lakes Riesling typicity. This type of study would benefit from replication over several vintages as 2009 was an atypically cool year in the region. While clone was found to be a main factor in determining phenolic acid profiles, limited research has been conducted on the effects of viticultural practices and vintage on hydroxycinnamic acids in Riesling.

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CHAPTER 3

FUTURE WORK

True to the nature of research, the work toward answering the question of whether Riesling grapes grown along the shores of Cayuga, Seneca, or Keuka Lakes results in Riesling wines with distinct sensory characteristics perceived by white wine consumers has generated even more questions. While the research thus far has contributed to the overall understanding of Finger Lakes Riesling terroir, this graduate thesis was merely the tip of the iceberg. Continuation of this work, as well as modified or companion studies, would aid progress toward elucidation of the impact of growing conditions and clone on wines produced from Finger Lakes Riesling.

This study would benefit from replication over several years, further investigating the vintage effect on Riesling typicity. While climate is one of the underlying components of terroir, weather trends are variable from vintage to vintage. This phenomenon can be especially important in cool-climate winegrowing areas where the weather is seemingly more variable and unpredictable. In the Finger Lakes, temperatures from spring through fall have the potential to impact length of the growing season as determined by accumulated GDD, or lack thereof. Likewise, cool and rainy vintages may result in different disease pressures and pest control regimes with potential to impact fruit quality. Thus, harvest decisions may be determined by impending frost or disease pressure rather than at the discretion of the vigneron. Repeating the study over multiple vintages would explore whether Rieslings produced from the same vineyard site differ according to vintage conditions, and if Rieslings produced from distinct sites across the Finger Lakes are more or less differentiated according to specific vintage conditions. Riesling wines were not

perceived as different in a cool and cloudy year, but the effects of a hot and dry year on different Riesling has yet to be determined.

In addition, a multi-year study would ensure proper standardization of the sites over time. Because the viticultural standardization commenced during the same growing season that the study was carried out, it is unclear whether latent effects from the previous growing season played a role in the sensory outcomes. For example, it is known that carbohydrate stores from the previous growing season are involved in the physiological processes in the beginning of the following growing season. Additionally, winter pruning could be standardized among sites.

A study that perhaps could have preceded this work is a survey of commercial Rieslings in the Finger Lakes. Conducting descriptive analysis on commercial Rieslings produced from different viticultural areas in the Finger Lakes would also sensorially assess Riesling typicity in the Finger Lakes. This type of study would investigate the hypothesis that Rieslings produced from different lakes have distinct sensorial characteristics. Further, viticultural areas could be defined in multiple fashions for various investigations: lake association, north-south orientation along the lakes, and association with the east or west sides of the lakes are merely three possible options. One challenge would be to confirm that the commercial Rieslings were actually produced from fruit in specific designations and of a common clone; it is not unusual for wineries to make Rieslings from fruit purchased around the Finger Lakes and blend parcels together. While this research would essentially ignore viticultural and winemaking practices, it would be most closely related to the informal sensory assessments of Finger Lakes Riesling upon which this original study was founded.

Because typicality goes hand in hand with regional growing conditions, sensory analysis on Finger Lakes Riesling should directly address this topic. Moreover, enologists, winemakers, and wine experts familiar with Finger Lakes Rieslings can be

involved in formally assessing whether experimental Rieslings are sensorially representative of the Finger Lakes. To this end, Riesling studies conducted on the experimental/research level can be appropriately related to the Finger Lakes region. Without such studies, results may be applied out of context.

One point mentioned above is the necessity to broaden the study to incorporate Rieslings from all areas of the Finger Lakes. In particular, viticultural sites on the west sides of the lakes were not included in this research, and further work is warranted to investigate potential differences comparing Rieslings grown on eastern and western lake slopes, as well as Rieslings produced from vineyards grown along the west sides of the lakes. Based on the results of this study, the wines produced from grapes grown on opposite lake shores may have more potential to produce significantly different Riesling profiles, as aspect may play a role in Finger Lakes terroir.

One soil variable that appears to set Riesling vineyards apart is soil pH. While pH amendments to the soil are common for vineyards not established on calcareous bedrock in the Finger Lakes, the soil pH variable still differentiated the vineyard sites. As there is an inherent soil pH trend which hinges on parent material from north to south, this characteristic may be worth investigating. The topic of soil characteristics brings up another issue. More intense work exploring the geology of the vineyards beyond the first 6 inches of topsoil may uncover other differences or similarities among vineyard sites. As grapevine roots can penetrate deep into the terrain for water and nutrients, it is possible that the soil profiles in this study did not capture the entire picture. A collaborative study between geologists, viticulturists, and enologists would best address this particular topic. Moreover, terroir studies incorporating GIS/GPS have been on the rise, and these technologies could be exploited in future studies on terroir.

In order to accommodate timelines, the sensory analysis of the wines in this study was conducted shortly after bottling. While some commercial wineries in the Finger Lakes release the previous vintage's Rieslings in early spring, others may hold onto Rieslings for up to one year for flavor development or other non-sensory related (logistical, business) reasons. Bottle aging undoubtedly impacts wine chemical and sensorial characteristics. It would be interesting to re-evaluate the same wines after a year in bottle and/or conduct a follow-up study comparing Finger Lakes Rieslings at different time points post-bottling. TDN and linalool have been shown to increase and decrease, respectively, in Rieslings over time, and the rates of change may result in distinct Riesling characteristics with age that could be linked back to terroir. Another route would be to analyze for potential TDN in the wines.

Since the phenolics data from this study revealed differences by clone with secondary terroir effects, further investigation seems worthwhile. The first step would be to characterize the remaining unknown phenolic acids detected by HPLC to confirm initial findings. Evaluation of juice would also provide support for the wine data by confirming that the effects are in fact related to clonal characteristics and not induced by the winemaking process. In general, future research on different clones growing in the same soil conditions and exposed to the same climatic events would simplify evaluation of the impact of clones on Finger Lakes Riesling. Additionally, future studies could focus on how different viticultural and enological practices influence chemical constituents and sensorial properties of Riesling.

Because the wines in this study were not found to be significantly different by descriptive analysis, one of the logical conclusions would be to assign winemaking practices as a major reason for differences perceived in commercial wines. In order to test this hypothesis, fruit from the individual vineyard sites could be vinified two ways: half of the fruit processed in-house according to a standard winemaking protocol, and the other half processed at the winemaker's discretion. Along similar

lines, standardizing musts prior to fermentation warrants consideration. The Brix and YAN levels were both adjusted in this study, and those variables may have confounded the results. If the wines are truly to reflect the site, it may be advisable to not add YAN to the musts, or add a fixed amount to all musts prior to fermentation. However, low YAN musts have detrimental implications for wine quality, and as more wineries analyze their juices for YAN levels and standardize accordingly, this consideration may become moot. A survey could be conducted in the Finger Lakes to gather information about winemaking practices (settling agents, yeast strains, etc.), and experimental studies can be designed accordingly so that results are applicable to the majority of industry. Obviously, this approach has its limitations as winery protocols are very individualized.

In the end, the Finger Lakes are known collectively as a region producing outstanding Rieslings. Thus, sensory analysis of Finger Lakes Rieslings together with Rieslings from other regions (Germany, Australia, etc.) will add to the overall understanding of Rieslings and how they reflect unique growing conditions.

In summary, several follow-up studies investigating vintage effects, winemaking influences, additional vineyard site locations, soil pH trends, bottle aging, etc. would shed more light on the impact of growing conditions on Riesling profiles in the Finger Lakes. Additionally, clone type can be tied into this research, but separate studies may be more effective in determining clonal effects on Riesling. However, due to the complex nature of enology and viticulture, experimental design and multivariate analyses seem critical for extracting meaningful research for practical application.